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Studies of lime sulphur and arsenate of lead for spraying

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STUDIES OF LIME SULPHUR AND ARSENATE OF LEAD FOR SPRAYING

by

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GENERAL SUMMARY OF STUDIES OF LIME SULPHUR AND ARSENATE OF LEAD FOR SPRAYING

1. The investigation is conducted in the Pomology Section of the Horticultural Department of the Iowa Agricultural Experiment Station.

2. A study is made of the methods of mixing in an attempt to ascertain the most favorable procedure (Part I); of the cause and prevention of injury (Part II); and of the effects of the spray films on the rate of growth (Part III), of lime sulphur and arsenate of lead.

3. In many cases unsatisfactory results in the application of the spray mixture often thought to be due to faulty machinery, improper pressure, clogging of spray nozzles, and conditions bringing about injury, such as excess of water-soluble arsenic, and presence of a soluble arsenate, are brought about by these factors indirectly because of an unsuitable method of mixing.

4. There is a difference in the amount of precipitate, color of precipitate, and color of solution when the same proportions of lime sulphur and arsenate of lead are used but mixed in a variety of ways.

5. When no supplemental material is used the most desirable method of mixing with reference to freedom from arsenical injury is to almost fill the tank with dilute lime sulphur

solution and then pour in the arsenate of lead powder mixed in a small amount of water.

6. Lime, either lump or hydrated, added to the dilute lime sulphur solution before the arsenate of lead, or mixed with it results in a decreased presence of arsenical substances injurious to fruit and foliage and shows a desirable grayish colored, small amount of sediment showing that but slight decomposition has taken place. The formation of the comparatively useless dark colored lead sulphide is checked. The use of caseinate leads to somewhat similar results.

7. Buttermilk, or skimmilk may be used to advantage as a spreader in the spray solution. As a source of casein they are considerably cheaper than the commercial caseinate. They do not clog the meshes of the screen in the spray tank, a trouble often caused by the commercial caseinate powder.

8. Boiling water in place of cold (24°C) results in a decreased amount of sediment, and causes more dry lime sulphur to be dissolved in a given length of time as is indicated by the increase in redness in color of the solution.

9. At times in the orchard the application of the solution results in an increased amount and severity of injury and in a variation in the amount of fungus diseases controlled. Various factors are intimately related with the lime sulphur type of injury indicating that the following theories, sometimes independently but often correlated with one another, are

responsible.

(a) The soluble polysulphides as the direct active agent.

(b) Absorption of the lime sulphur by the chlorophyll.

(c) Sunlight.

(d) Heat.

(e) Gas.

(f) Acid.

(g) Oxidation.

(h) Minuteness of sulphur particles.

10. Sunlight, heat, and oxidation may independently cause discoloration in leaves similar to lime sulphur injury. When exerting a detrimental effect at the same time as lime sulphur the injurious action is accelerated.

11. Experiments in the laboratory and observations in the orchard indicate that the factors conducive to, and correlated with the lime sulphur spray solution destruction of chlorophyll are high pressure, forcibly driven and coarse sprays, conditions leading to a thin epidermis, reduction of pubescence, loose internal structure, presence of nascent oxygen, strong sunlight liberating actinic rays and heat, and subsequent final killing and oxidation of the tissues.

12. A microscopical examination of leaves damaged by lime sulphur indicates that the injury first appears as a slight russetting on the under surface. The injurious sub-

stance enters through the stomata and within 24 hours causes a brown coloration extending to the upper surface.

13. Very minute particles of sulphur are given off from liquid lime sulphur. Leaves and algae subjected to this form of sulphur are killed, while the comparatively large particles of finely divided flowers of sulphur exert no injurious effects under the experimental conditions. Apparently direct injury from sulphur is correlated largely with the minuteness of the size of particle.

14. Sulphur dioxide and hydrogen sulphide gases are liberated from liquid lime sulphur. These gases on combination with water give an acid reaction. The formation of acid from liquid lime sulphur from the union of these substances at room temperatures is very gradual.

15. Sulphuric acid could not be detected in appreciable quantities in or as being liberated from lime sulphur. Apple fruits and leaves, however, when sprayed with sulphuric acid, 1 - 1000, show effects similar to lime sulphur injury.

16. Orchard trials show the fungicidal value of sulphuric acid, 1 - 1000, to be nil as fungus diseases and insect pests are not controlled. Extensive injury also occurs.

17. Spray films of lime sulphur, arsenate of lead, and the combination of the two, exert an influence on the rate of growth of plants; being distinct in this respect from their fungicidal and insecticidal actions.

18. Transpiration and photosynthesis are two factors closely concerned with this modification in structure.

19. Aqueous solutions of arsenate of lead, and of arsenate of lead and lime sulphur mixed, when applied to the foliage of plants, cause an increase in transpiration. Lime sulphur solution alone has little effect.

20. The greatest transpiration in this investigation takes place two to three hours after spraying, or at 11 o'clock independent of spraying.

21. The minimum water content of the leaves occurs at about 1 o'clock. The percentage moisture in the leaves decreases from daybreak until this time, and then increases again.

22. When a spray film of lime sulphur is applied to the foliage of tomato plants less organic material is formed, other factors being equal, than when water is applied as the spray. Arsenate of lead, and the mixture of lime sulphur and arsenate of lead increase the amount of organic material formed, during the same length of time and under similar external conditions.

23. The rate of growth of plants following applications of the spray mixtures is influenced by the amount of water transpired, and the amount of materials formed by photosynthesis in the leaves.

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There is perhaps no phase of orchard management that requires so much attention and gives such varying results as the spraying of the trees to protect them against the ravages of insect pests and fungus diseases. When nature's part in preparing for a bountiful crop is done the percentage of marketable fruit produced is determined largely by the kind of spraying given. The variation of results due to different methods and materials as well as the ever changing atmospheric effects, leads to many experiments for the purpose of finding a spray material which will give good results under any and all conditions.

Lime sulphur mixture is attracting considerable attention and nearly every college experiment station has literature available showing its insecticidal and fungicidal properties during the last decade. It has practically no value as a stomach poison for biting insects so arsenate of lead is added. In addition to its insecticidal value it is found that the arsenate of lead has some value as a fungicide.

EXTENT OF STUDIES

This study comprises researches of the reasons why the lime sulphur-arsenate of lead combination spray does not always give the results desired, and means by which its beneficial properties may be improved and injurious effects reduced

to a minimum. The present investigations at Iowa State College are carried on during the colder months in the Botanical and Chemical laboratories. Certain observations are also made in the greenhouses during this period. The remainder of the season is spent in practical orchard application of the results obtained in the laboratory. The studies during the summer months are carried on in the orchards of the Pomology Experiment Section of the Horticultural Department.

Tests are made of the various ways in which the lime sulphur and arsenate of lead may be mixed in an attempt to ascertain the optimum method, special attention being paid to certain physical and chemical aspects of the amount and color of precipitate and color of solution. The value of lime as supplemental material for the prevention of arsenical injury is investigated in relation to its physical and chemical effects, and certain casein containing compounds are tried out as spreaders in the usual lime sulphur-arsenate of lead sprays.

The factors influencing the fungicidal powers and injurious effects of lime sulphur are studied and an attempt made to link up the independent theories in vogue, and also to investigate the most promising ones more fully.

Finally, the effects of spray films of lime sulphur, arsenate of lead, and the mixture of the two, are discussed in relation to their influence on the rate of growth of plants.

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General Chemical Company, 25 Broad St., New York.

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PART I

THE MIXING OF LIME SULPHUR AND ARSENATE OF LEAD

A very practical problem confronting fruit growers using the combination spray of lime-sulphur and arsenate of lead is the question of the best way of mixing the two substances. Unfortunately, the mixing of lime sulphur and arsenate of lead while apparently a simple matter is carried on by most orchardists in a more or less haphazard manner. In many cases unsatisfactory results in the application of the spray mixture often thought to be due to faulty machinery, improper pressure, clogging of spray nozzles, and conditions bringing about injury, such as excess of water-soluble arsenic, and presence of a soluble arsenate, are brought about by these factors indirectly because of an unsuitable method of mixing. Not realizing that there is a difference the orchardist pays little attention to the method used in mixing his spray materials and seldom do we find a continued duplication in the mode of combination. Some men prefer to fill up the spray tank with the water and lime sulphur before adding the arsenate of lead slaked in a small amount of water. Others claim advantages when the lime sulphur and arsenate of lead are both added to the tank before the required amount of water is put in. Still further methods of mixing are sometimes advocated. It is because orchardists are not unanimous in opinion as to the most favorable method of combining the two

substances that this phase of study is undertaken.

HISTORICAL

Considering that spraying is one of the most important messages that the experiment station has to offer the fruit grower, a critical survey of the literature reveals the fact that the problem of mixing lime sulphur and arsenate of lead is not given the attention deserved. In practical orchard work it soon becomes known that the least amount of difficulty in mixing the two materials occurs when the arsenate of lead is added as the final substance to the spray solution. This certainly is convenient but no systematic work is available showing it to be the optimum method of mixing.

Reflection of the methods of manufacture of that rival fungicide of lime sulphur viz. Bordeaux, draws attention to a common classroom test. The materials being united as follows:

(a) The copper sulphate is dissolved in almost the total volume of water, and the lime added last.

(b) The lime is slaked, water is added to almost the total volume, and the copper sulphate added last.

(c) The lime is slaked in one-half the total volume of water. The copper sulphate dissolved in one-half the total volume of water and the two poured together at one time.

When mixed in these three ways in the laboratory the last method apparently is the most efficient in keeping the materials in suspension longest. However, in orchard work it is more convenient to make up stock solutions of the lime and of the copper sulphate and depend upon mechanical agitation of the solution for suspension of the particles.

The color of the precipitate of the lime sulphur-arsenate of lead mixture denotes to a certain extent the chemical changes occurring. As the result of studies on the decomposition of lead arsenates when combined with lime sulphur, Robinson (58)* finds, "The residue from acid lead arsenate was dark in color due to presence of lead sulphide. Residue from basic was gray indicating but slight decomposition."

As the reader proceeds the impression should be gained that a gray colored precipitate such as is found when the basic lead arsenate is used is the desired one. But the basic lead arsenate is not readily available for orchard spraying as Lovett (40) points out that, "The commercial lead arsenates on the market, unless specifically prepared and labeled otherwise, are nearly pure acid lead arsenate."

Since the basic lead arsenate is not procurable other means are taken to secure similar results with other substances.

Arsenate of lead is added to lime sulphur solution for the control of biting insects and hence the amount of the compound necessary for this purpose is of importance. In this connection Lovett (40) shows that 1 pound of the acid

* Numbers in parenthesis refer to Literature Cited, p. 144

lead arsenate to 400 gallons of water is a sufficient dose for small caterpillars. He does not recommend this proportion for orchard use but the point of interest here is that but a very small amount of the arsenical compound is actually necessary as a stomach poison for the types of insects usually met with in the fruit plantation. Allowing for the natural factors which render ideal conditions impossible in commercial orchard spraying, Lovett (40) finds that the apparent discrepancy between the theoretical killing dosage of arsenate of lead and the standard dosage in vogue is due in part to physical effects:

> "(a) In the method of application of the spray.
> (b) In the spray solution.
> (c) In the spray material."

Sanders (63) points out that, "Lime sulphur reduces the killing value of poisons by 15 to 20 percent, an amount which is negligible in practice."

From a chemical standpoint when arsenate of lead is combined in solution with lime sulphur Ruth (60), and Robinson (57) agree that there is a decrease of sulphur and of calcium in solution, and that the formation of lead sulphide occurs. Cory (16), and Robinson (57) also show that on the combination of lime sulphur and lead arsenate there is a decrease of calcium in solution; the acid lead arsenate being more active in this respect.

In reference to the color of solution Safro (61) writes as follows: "The depth and color of the lime sulphur solution increases with the polysulphides in solution."

The efficiency of the lime sulphur solution is to a large extent supposed to be due to the percentage of soluble calcium polysulphides present; the higher the percentage of the soluble polysulphides present the greater the value of the solution. Safro (61) says, "The property of causing injury is located, for the most part, in the soluble phlysulphides. A color test, though not practical for the fruit grower, would be more accurate than a specific gravity test."

The factor of acidity of solution is given scant attention in spray investigations and no data as yet is available bearing directly on the lime sulphur and arsenate of lead combination solution. McDonnell and Graham (45) show that, "Dilead arsenate of lead is decomposed by water. This means more than that it simply goes into solution. The reaction proceeds with the liberation of arsenic acid and the solution of a very small quantity of lead. The reaction reaches equilibrium while the concentration of arsenic acid is very low, but if the water is not constantly changed, it proceeds until the residue is converted to a definite basic arsenate."

Volck (75) claims that arsenate of lead is slightly more soluble in alkaline than in acid solution and believes that after the arsenate remains for a short time in water the solution will give an acid reaction and shows that by this change a more highly insoluble compound is secured. In this form it is less injurious to the plant.

It is sometimes thought that because lime is used in the manufacture of the lime sulphur mixture that the resulting solution will be alkaline in nature. No doubt tests made

with litmus paper tend to the general impression that the solution is not acid in reaction. But with the advent of apparatus more accurate than litmus paper for the determination of acidity a clearer insight into this factor may be gained.

The addition of lime as a supplemental material to the mixture of lime sulphur and arsenate of lead is known to have been advocated for some time but is not widely followed in general practice. Crandall (17) mentions that in 1889, even before arsenate of lead had been established as a valuable orchard spray material, Gillette found that the addition of lime to compounds of arsenic greatly reduced the injury to foliage. In this connection it may be recalled that the use of lime is recommended by companies selling spray materials to be mixed with arsenate of lead when used alone in water on peach trees. Van Slyke et al, (74) state on the effects of adding lime to diluted lime sulphur at the rate of 10 pounds to 50 gallons added to 1-8 solution that, "The amount of sulphide sulphur was decreased while CaS_2O_3 was increased with formation of free S. The changes thus caused may be so great as to seriously decrease the insecticidal power of the mixture."

However, the fungicidal properties of the lime sulphur are of more concern than the insecticidal powers in the Stat of Iowa and since Haywood (29) shows that the calcium thiosulphate, sulphites, and the free sulphur are the active agents in this respect the value of lime is obvious.

On the employment of lime as a supplemental material in the dry lime sulphur and arsenate of lead spray Chase (14) writes, "(1) It improves the physical properties of the mixture by eliminating the lumps that occur in mixtures of sulphur and arsenate of lead, thus allowing the mixture to flow more uniformly through the nozzle.
(2) Being cheap, it reduces the cost by displacing the more expensive sulphur, the injurious effects of which it also tends to neutralize."

Delayed injury from the lime sulphur-arsenate of lead spray mixture is shown by Wallace (76), and Hewitt (31) to be due to arsenical burning.

When arsenate of lead is mixed with lime sulphur solution Robinson (57) concludes, "Calculated from the original amount of lead hydrogen arsenate used, over 5 percent of the arsenic was found in a soluble form thus increasing the tendency to cause burning of foliage and other injury. Furthermore, the decrease in the sulphur content indicates excessive loss of that active element."

Riches (56) of the Riches-River Company writes that, "From a chemical standpoint lead arsenate apparently is not the best arsenical to combine with lime sulphur. Both materials are broken up and, under certain conditions, you will have present a soluble arsenate. Curiously enough, this condition is present when the arsenate of lead is mixed with very dilute lime sulphur. The lead arsenate is decomposed and there is not enough lime available to form the insoluble arsenate."

According to Sanders (64) , "Lime sulphur reduced the killing value of poisons by 15 to 20 percent an amount which is negligible in practice. When large quantities must be used against biting insects, it has been found injurious to the foliage to add large quantities of fungicides to them, as the lead arsenate so used breaks up and forms so much soluble arsenic."

On investigating means for the prevention of this type of injury Robinson (57) finds that, "The presence of free lime prevents arsenic from going into solution as a soluble salt. Where no lime was added a usual high percentage of soluble arsenic was found indicating that over 18 percent of the lead hydrogen arsenate was decomposed, decreasing its efficienty accordingly. Observation of the changes that occurred during the reaction showed that those samples treated with lime slowly turned to a gray color similar to the basic lead arsenate and lime sulphur mixture where the amount of chemical changes was negligible, while those untreated immediately turned black, indicating the breaking down of both lime sulphur and arsenate of lead and the formation of lead sulphide. The polysulphide content of the combination spray that had been treated with lime had decreased only a negligible amount, while the untreated showed a loss of almost 50 percent of its fungicidal properties. Attention is further called to chemical changes that had continued during the two days; where no lime had been added previously to the combination spray over 75 percent of the lime sulphur remained unchanged and as efficient as ever for spraying purposes. Where no lime had been added all polysulphide sulphur had been transformed into lead sulphide or to thiosulphate. In this form the spray is practically valueless as its peculiar properties are destroyed."

As the outcome of his chemical investigations Robinson (57) advocates the use of 10 pounds of lime to 100 gallons of lime sulphur before the addition of arsenate of lead to the solution. After further study he recommends (58) that, "The lime sulphur should be introduced into the tank and after diluting to the strength to which it is to be applied about 2 pounds of good quick lime are made into milk of lime and poured into the tank. The lead arsenate is then added. It is important that the lime sulphur diluted and the quick lime be first mixed before introducing the arsenate of lead."

Fruit growers in the Pacific coast section are apparently looking with favor upon the use of spreaders in

their spray solutions. Lovett (40) defines spreaders as materials added for the purpose of improving the physical properties of the spray solution:

"(a) By increasing the wetting and covering power of the spray solution.
(b) By increasing its adhesiveness."

The advantages of spreaders are given by Lewis (36) as follows:

"(a) Better protection of fruit and foliage.
(b) Increased efficiency of the spray.
(c) Less opportunity or danger from spray injury.
(d) Greater economy - spray would go farther.
(e) Reduced visibility of spray on fruit.
(f) No wiping required.
(g) Less danger of removal of spray in fall by heavy rains, as the spray tends to gather in big drops and to fall to the ground from these large drops.
(h) More adhesiveness of spray.
(i) Specially valuable for light spray materials.
(j) Show to better advantage where the lower power outfits are used."

Lovett (40) considers the qualities of spreaders desired to be:

(1) Availability - the source of supply must be adequate.
(2) Compatability - they must not react unfavorably with any ordinary spray material or combination of spray materials.
(3) Efficacy - in reasonable amounts they must actually give satisfactory results.
(4) Ease of preparation - complicated formulae, cooking, any operation requiring much close or additional work meets little favor among our growers.
(5) The cost must be reasonable.

It is interesting to note that what is perhaps the earliest work on the increase of spread and adherence in sprays in this country may be claimed for the State of Iowa.

The investigations of Gillette (28) show that these factors were seen to be of importance when the use of spray materials in solution was still in a pioneer stage in this country.

Casein is attracting considerable attention as a substance for increasing spread and adherence. Mellanby (46) states that, "Casein is the protein precipitated from milk by the action of proteolytic ferments and calcium salts."

Thorpe (73) relates that, "Cow's milk, which is its only commercial source, contains on an average about 3 percent casein."

Commercial casein spreaders first appeared on the market in 1921. The powders represent a high grade casein, ground somewhat finer than the ordinary commercial product and thoroughly mixed in definite proportions with hydrated lime. Practically all the casein in milk may be obtained in skimmilk or buttermilk, and since either of these substances is readily obtainable in liquid form in any section of Iowa the fruit grower may procure casein from this source at very moderate prices.

According to Scherer (67), "It is always advisable to add to the casein a little sodium arsenate, Na_2HAsO_4, or some other salt of arsenic, since this increases the adhesive power and forms a kind of chemical mordant." The effect of the arsenate of lead, which is an arsenical salt, may for this reason increase the adhesiveness of the lime sulphur-lead arsenate-casein mixture.

The theories of spreading and adherence are summarized very clearly, as is also the survey of the literature by Moore (49). In his investigational work with arsenicals he finds that, "The leaf surface when wet, exhibits a negative electric charge, and that suspensoids of the common arsenic compounds ionize in such a way that their particles are also negative. Based upon the results obtained in the dye industry, the assumption is made that spray materials carrying positive electric charges would adhere to the negatively charged leaf surface better than particles exhibiting negative charges.

> Organic materials which produce a film of the spray on the surface of waxy leaves should have no influence on the electric charge, but the protein type of spreader may have a decided effect. Since most emulsoids, such as gelatin, casein, and proteins act as protective colloids, their addition to the spray might result in the complete loss of the electric charge. On the other hand, a mutual precipitation may occur (Bancroft, (4), or if the positive charges are in excess the material may retain its positive character. Only field tests will solve these problems."

With regards to the employment of spreaders and with reference to the amount of arsenical compound necessary in the mixture, Lovett (40) writes as follows:

> "By increasing the wetting and covering powers of the solution it permits us to reduce the amount of arsenic necessary for protection. By permitting a more uniform covering over the surface and increasing the adhesiveness it affords a better protection from worms."

METHODS OF EXPERIMENTATION

In attacking the problem relative to the best way of uniting the lime sulphur and arsenate of lead the study is made from two standpoints, viz.,

(a) Physical

(b) Chemical

(a) PHYSICAL:

In the laboratory the materials are mixed in the various ways and after being well stirred once are allowed to settle for examination in 600 c.c. hydrometer, glass jars, the tests being made in duplicate. The proportions used are as follows:

Liquid lime sulphur.....	12.5 c.c.
Dry lime sulphur.....	6.5 grams
Arsenate of lead (powder).....	2.0 "
Lump lime.....	2.0 "
Hydrated lime.....	2.0 "
Caseinate.....	2.0 "
Liquid buttermilk.....	3.25 "

Tap water is used in all the trials, cold (24° C), and at boiling temperatures. Readings are taken 2, 5, 60, and 120 minutes after mixing. Measurements of the amount of precipitate are made with a centimetre rule. The color

determinations are made by comparison with water color charts made for this purpose. The coloration shown represents the appearance of the precipitate or solution as seen through the glass of the hydrometer jar. While the color of the solution could be obtained by direct comparison of the liquid and water color, it is not practicable to illustrate the color of the precipitate by this means and hence the method as given is adopted throughout. Each method of mixing is given a number and is represented throughout the rest of the work by this number.

TABLE 1

INDEX REFERRING TO NUMBERS DENOTING METHODS OF MIXING

LIQUID LIME SULPHUR SERIES:

Number 1:

(a) The lump lime is slaked in 50 c.c. of water.

(b) The concentrated lime sulphur is added to (a).

(c) 387.5 c.c. of water are poured into (a + b).

(d) The arsenate of lead is dissolved in 50 c.c. of water and then poured into (a + b + c).

Number 2:

(a) The arsenate of lead is dissolved in 50 c.c. of water.

(b) 437.5 c.c. water are added to (a).

(c) The concentrated lime sulphur is then poured into (a + b).

Number 3:

(a) The concentrated lime sulphur is diluted in 500 c.c. water.

(b) The arsenate of lead powder is dumped into (a).

Number 4:

(a) The hydrated lime is slaked in 50 c.c. of water.

(b) The concentrated lime sulphur is added to (a).

(c) 387.5 c.c. of water are poured into (a + b).

(d) The arsenate of lead is dissolved in 50 c.c. of water and added to (a + b + c).

Number 5:

(a) 387.5 c.c. of water are poured into the jar.

(b) The concentrated lime sulphur is added to (a).

(c) The arsenate of lead is dissolved in 50 c.c. of water, and dumped into (a + b).

Number 6:

(a) The concentrated lime sulphur is diluted in 450 c.c. of water.

(b) The arsenate of lead is dissolved in 50 c.c. of water, and added to (a).

Number 7:

(a) The concentrated lime sulphur is diluted in 250 c.c. of water.

(b) The arsenate of lead is dissolved in 250 c.c. of water.

(c) (a) and (b) are poured together through a funnel.

Number 8:

(a) The concentrated lime sulphur is poured into the jar.

(b) The arsenate of lead is dissolved in 50 c.c. of water and added to (a).

(c) Water is added to the 500 c.c. mark.

Number 9:

(a) The concentrated lime sulphur is diluted in 400 c.c. of water.

(b) The lump lime is slaked in 50 c.c. water and added to (a).

(c) The arsenate of lead is dissolved in 50 c.c. of water and poured into (a + b).

Number 10:

(a) The concentrated lime sulphur is diluted in 250 c.c. of boiling water.

(b) The arsenate of lead is dissolved in 250 c.c. of boiling water.

(c) (a) and (b) are poured together through a funnel.

Number 11:

(a) The concentrated lime sulphur is diluted in 400 c.c. of water.

(b) The hydrated lime is slaked in 50 c.c. of water and added to (a).

(c) The arsenate of lead is dissolved in 50 c.c. of water and poured into (a + b).

Number 12:

(a) The concentrated lime sulphur is diluted in 400 c.c. of water.

(b) The arsenate of lead is dissolved in 50 c.c. of water and added to (a).

(c) The hydrated lime is slaked in 50 c.c. of water and poured into (a + b).

Number 13:

(a) The lime sulphur is diluted in 400 c.c. of water.

(b) The arsenate of lead is dissolved in 50 c.c. of water and added to (a).

(c) The lump lime is slaked in 50 c.c. of water, and poured into (a + b).

Number 14:

(a) The concentrated lime sulphur is diluted in 200 c.c. of water.

(b) The arsenate of lead is dissolved in 200 c.c. of water.

(c) The caseinate is dissolved in 100 c.c. of water and added to (b).

(d) (a) and (b) are then poured together thru a funnel.

Number 15:

(a) The concentrated lime sulphur is diluted in 200 c.c. of water.

(b) The caseinate is dissolved in 100 c.c. of water and added to (a).

(c) The arsenate of lead is dissolved in 200 c.c. water.

(d) (a + b) and (c) are then poured together through a funnel.

Number 16:

(a) The concentrated lime sulphur is diluted in 450 c.c. of water.

(b) The arsenate of lead is dissolved in almost 50 c.c. of water and added to (a).

(c) The liquid buttermilk is added to (a + b).

Number 17:

(a) The concentrated lime sulphur is diluted in 450 c.c. of water.

(b) The liquid buttermilk is added to (a).

(c) The arsenate of lead is dissolved in 50 c.c. of water and added to (a + b).

DRY LIME SULPHUR SERIES

Number 18:

(a) The lime sulphur is dissolved in 250 c.c of water.

(b) The arsenate of lead is dissolved in 250 c.c. of water.

(c) (a) and (b) are poured together through a funnel.

Number 19:

(a) The lime sulphur is dissolved in 50 c.c. of water.

(b) The arsenate of lead is dissolved in 50 c.c. of water.

(c) (a) and (b) are poured together thru a funnel.

Number 20:

(a) 400 c.c. of water are poured into the jar.

(b) The lime sulphur is dissolved in 50 c.c. of water and added to (a).

(c) The arsenate of lead is dissolved in 50 c.c. of water and added to (a+b).

Number 21:

(a) The arsenate of lead is dissolved in 450 c.c. of water.

(b) The lime sulphur is dissolved in 50 c.c. of water and added to (a).

Number 22:

(a) The lime sulphur is dissolved in 400 c.c. of water.

(b) The arsenate of lead is dissolved in 50 c.c. of water, and added to (a).

(c) The lump lime is dissolved in 50 c.c. of water, and added to (a + b).

Number 23:

(a) The lime sulphur is dissolved in 400 c.c. of water.

(b) The arsenate of lead is dissolved in 50 c.c. of water and added to (a).

(c) The hydrated lime is dissolved in 50 c.c. of water and added to (a + b).

Number 24:

(a) The lime sulphur is dissolved in 400 c.c. of water.

(b) The lump lime is dissolved in 50 c.c. of water and added to (a).

(c) The arsenate of lead is dissolved in 50 c.c. of water and added to (a + b).

Number 25:

(a) The lime sulphur is dissolved in 400 c.c. of water.

(b) The hydrated lime is dissolved in 50 c.c. of water and added to (a).

(c) The arsenate of lead is dissolved in 50 c.c. of water, and added to (a+b).

Number 26:

(a) The lump lime is slaked in 50 c.c. of water.

(b) The lime sulphur is added to (a).

(c) Water is added to the 450 c.c. mark to (a+b).

(d) The arsenate of lead is slaked in 50 c.c. of water, and added to (a+b+c).

Number 27:

(a) The hydrated lime is slaked in 50 c.c. of water.

(b) The lime sulphur is dissolved in 50 c.c. of water, and added to (a).

(c) Water is added to the 450 c.c. mark to (a+b).

(d) The arsenate of lead is slaked in 50 c.c. of water and added to (a+b+c).

In the field experiments the two rows of 20 year old trees in Orchard E, Pomology Section, Ames, Iowa, are taken and divided into four plots. Distance between trees in row equals 18 feet. Distance between rows equals 25 feet.

Plot III	Plot I
Malinda	Iowa Blush
Malinda	Unknown
	Iowa Blush
Walbridge	Ben Davis
Red June	Ben Davis
	Ben Davis
Red June	

Plot IV	Plot II
Oldenburg	Jonathan
Oldenburg	Gano
Oldenburg	Coles Quince
Wealthy	Pewaukee
Wealthy	

The plots were sprayed, (1) on May 1, with a Bean Giant Duplex sprayer, at 200 pounds pressure. The day was rather unsettled with a fairly strong wind blowing from the southwest, and little sunshine; during the night a heavy rain occurred. (2) On May 15, the weather was cool with scarcely any sunshine. (3) On June 3, weather fine, and also for the week following.

Plot 1

Water	50 gallons
Liquid lime sulphur	1½ "
Liquid buttermilk	2⅔ pounds
Arsenate of lead	1 pound

The lime sulphur is placed in the tank; the buttermilk added to the 50 gallons of water and pumped into the tank; then the arsenate of lead in one-half pailful of water is poured in.

Plot 2

Water	50 gallons
Liquid lime sulphur	1½ "
Caseinate	1/4 pound
Arsenate of lead	1 "

The lime sulphur is placed in the tank; the 50 gallons of water are pumped in; the caseinate is mixed in one-half pailful of water and carefully poured in, and then the lead arsenate is prepared in a similar manner and added.

Plot 3

Water	50 gallons
Liquid lime sulphur	1½ "
Hydrated lime	1 pound
Arsenate of lead	1 "

The materials are mixed as under Plot 2.

(b) CHEMICAL.

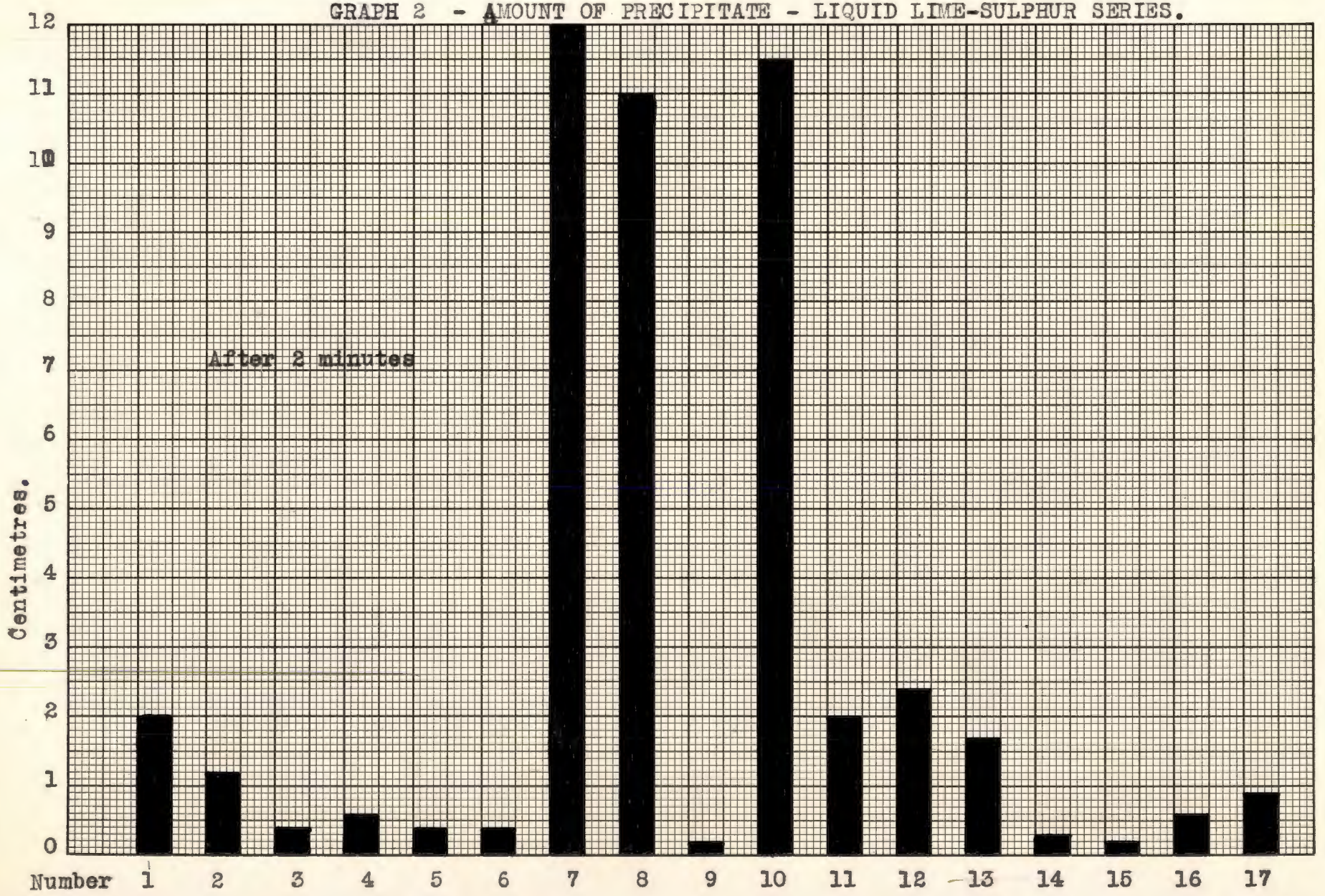
Enough of the clear solution is poured into a 125 c.c. beaker as to give there a liquid from one-fourth to one-half inch in depth, one-half hour after mixing. Hydrogen-ion determinations are then made for actual acidity, initial readings only being taken. Wendt's Electrotitration apparatus is used throughout. The results in each case are the average of several readings but because of the fluctuations evidenced are only approximate in nature.

Volak's (76) ammonia test is applied for the detection of excess injurious arsenical compounds. In this test the material is boiled in ammonia water. After cooling the solution is filtered. The filtrate is then acidified with acetic acid, and tested with lead acetate for the presence of a white precipitate.

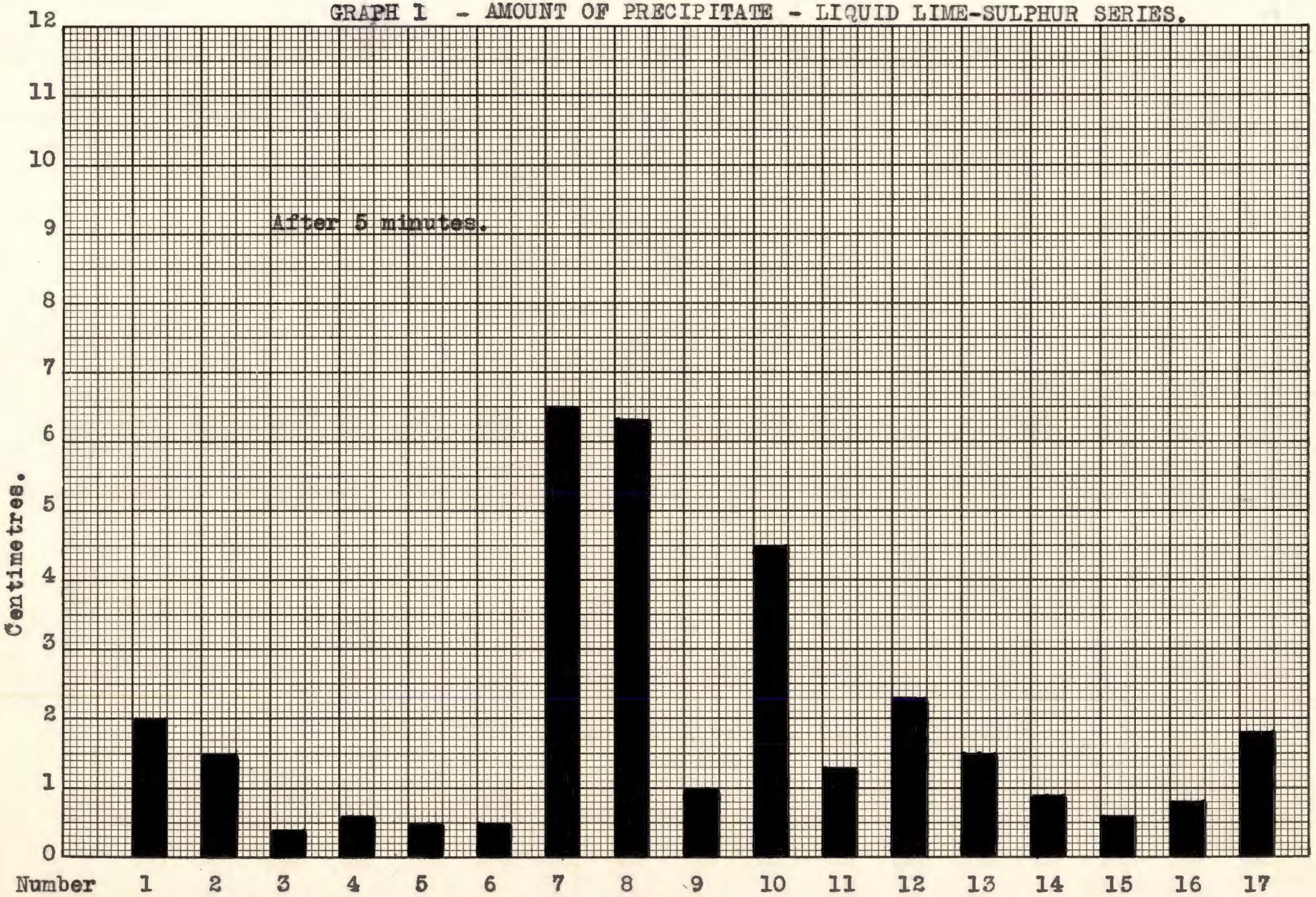
TABLE 2 - AMOUNT OF PRECIPITATE - LIQUID LIME SULPHUR SERIES

Mixture Number	cm. 2 min	cm. 5 min	cm. 60 min	cm. 120 min
1	2.5	2.0	2.0	2.0
2	1.7	1.5	1.5	1.3
3	.4	.4	.5	.5
4	.6	.6	.8	1.1
5	.4	.5	.6	.7
6	.4	.5	.6	.7
7	12.0	6.5	1.9	1.8
8	11.0	6.2	1.8	1.8
9	.2	1.0	1.2	1.2
10	11.5	4.5	2.2	2.2
11	2.0	1.8	1.5	1.5
12	2.4	2.3	1.5	1.4
13	1.7	1.5	1.2	1.2
14	.3	.9	1.0	1.0
15	.2	.6	.7	.8
16	.6	.8	1.0	1.0
17	.9	1.8	2.2	2.2

GRAPH 2 - AMOUNT OF PRECIPITATE - LIQUID LIME-SULPHUR SERIES.



GRAPH 1 - AMOUNT OF PRECIPITATE - LIQUID LIME-SULPHUR SERIES.



GRAPH 1 - AMOUNT OF PRECIPITATE - LIQUID LIME-SULPHUR SERIES.

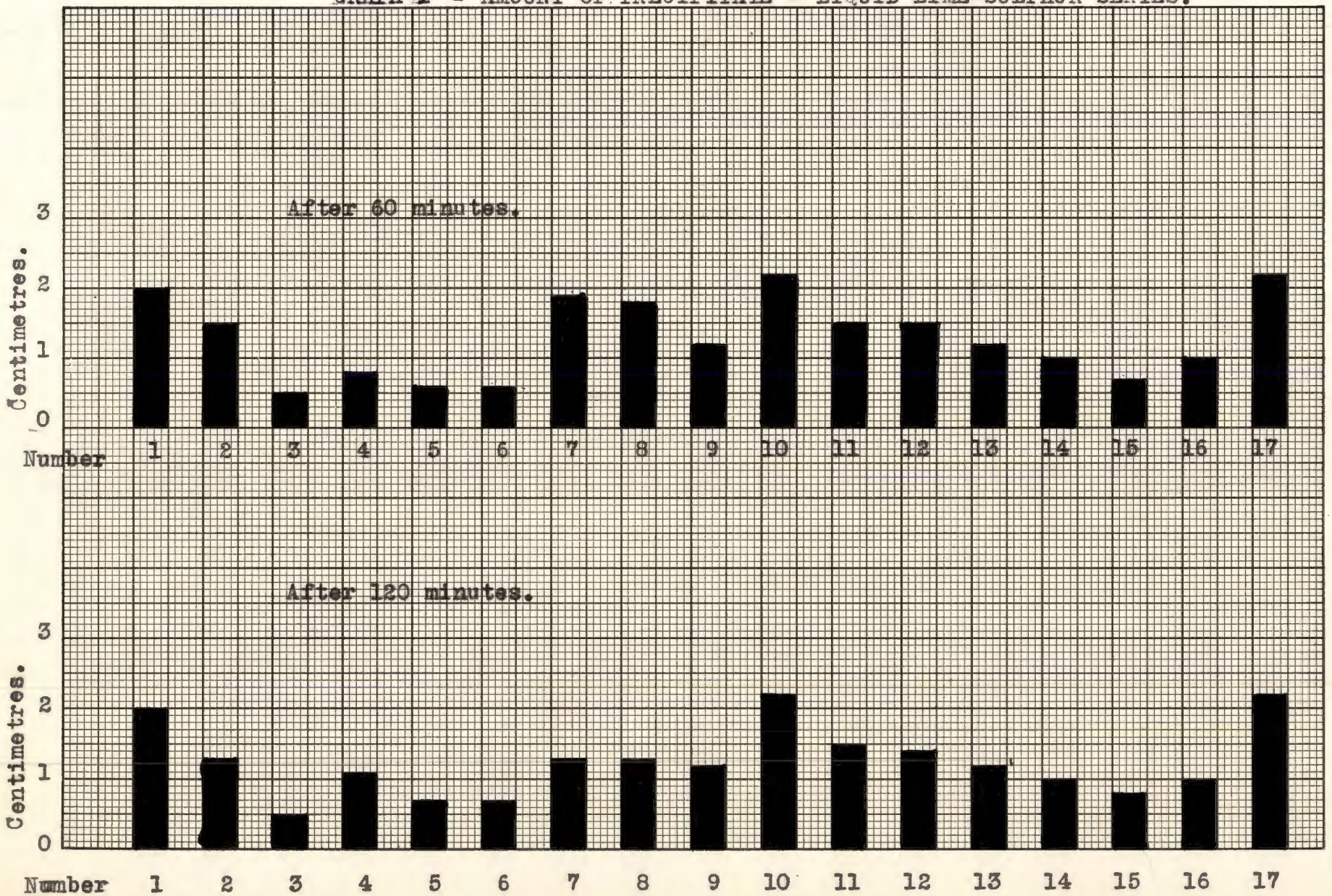
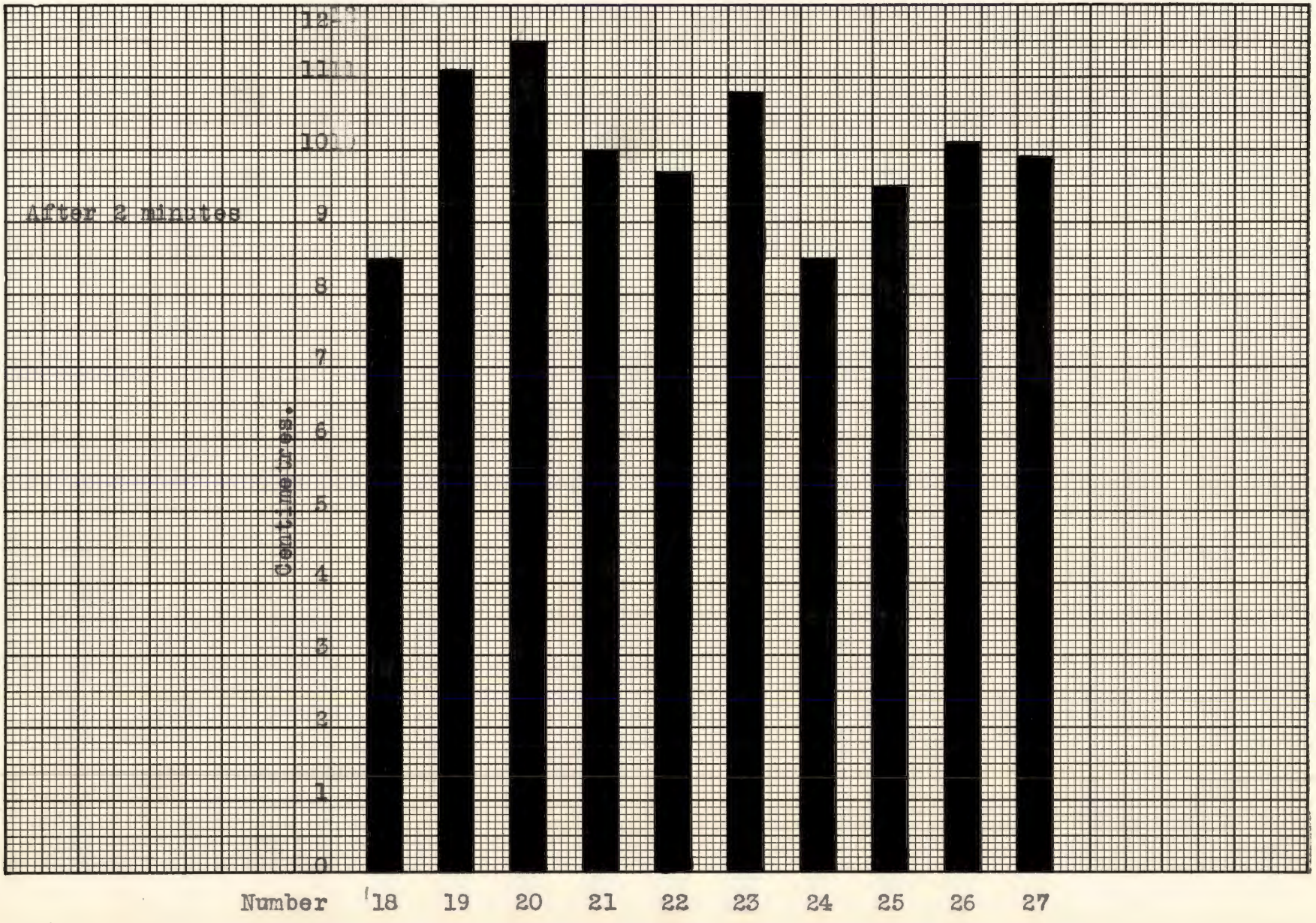


TABLE 3 - AMOUNT OF PRECIPITATE - DRY LIME SULPHUR SERIES

Mixture Number	cm. 2 min	cm. 5 min	cm. 60 min	cm. 120 min
18	8.5	5.3	3.0	2.8
19	11.1	7.3	4.1	3.8
20	11.5	6.6	3.5	2.8
21	10.0	6.8	3.8	3.8
22	9.7	5.9	3.0	2.9
23	10.8	6.7	3.6	3.4
24	8.5	5.5	2.5	2.4
25	9.5	6.4	2.6	2.5
26	10.1	6.8	3.0	2.8
27	9.9	6.6	3.0	2.8

GRAPH 2 - AMOUNT OF PRECIPITATE - DRY LIME-SULPHUR SERIES.



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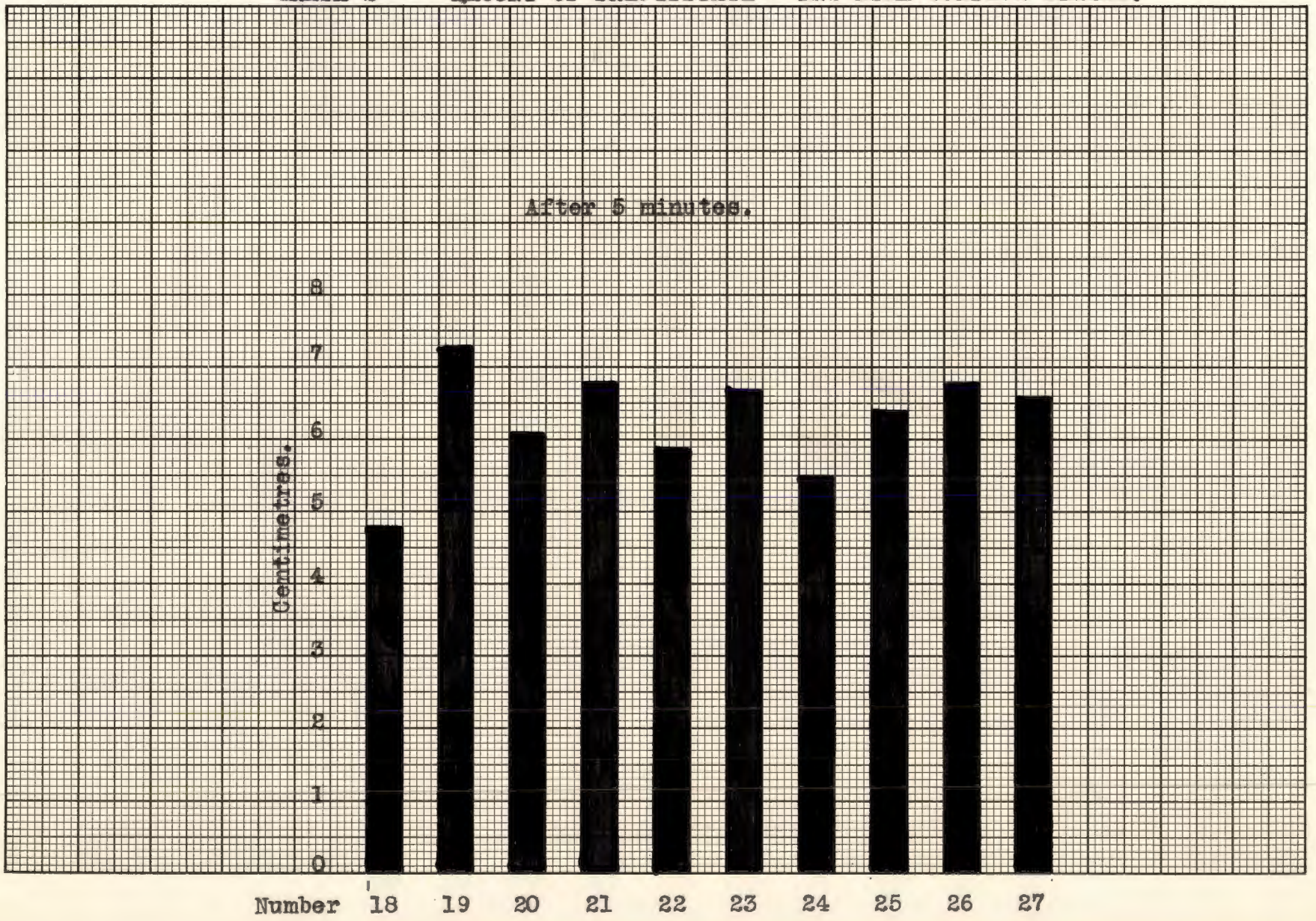
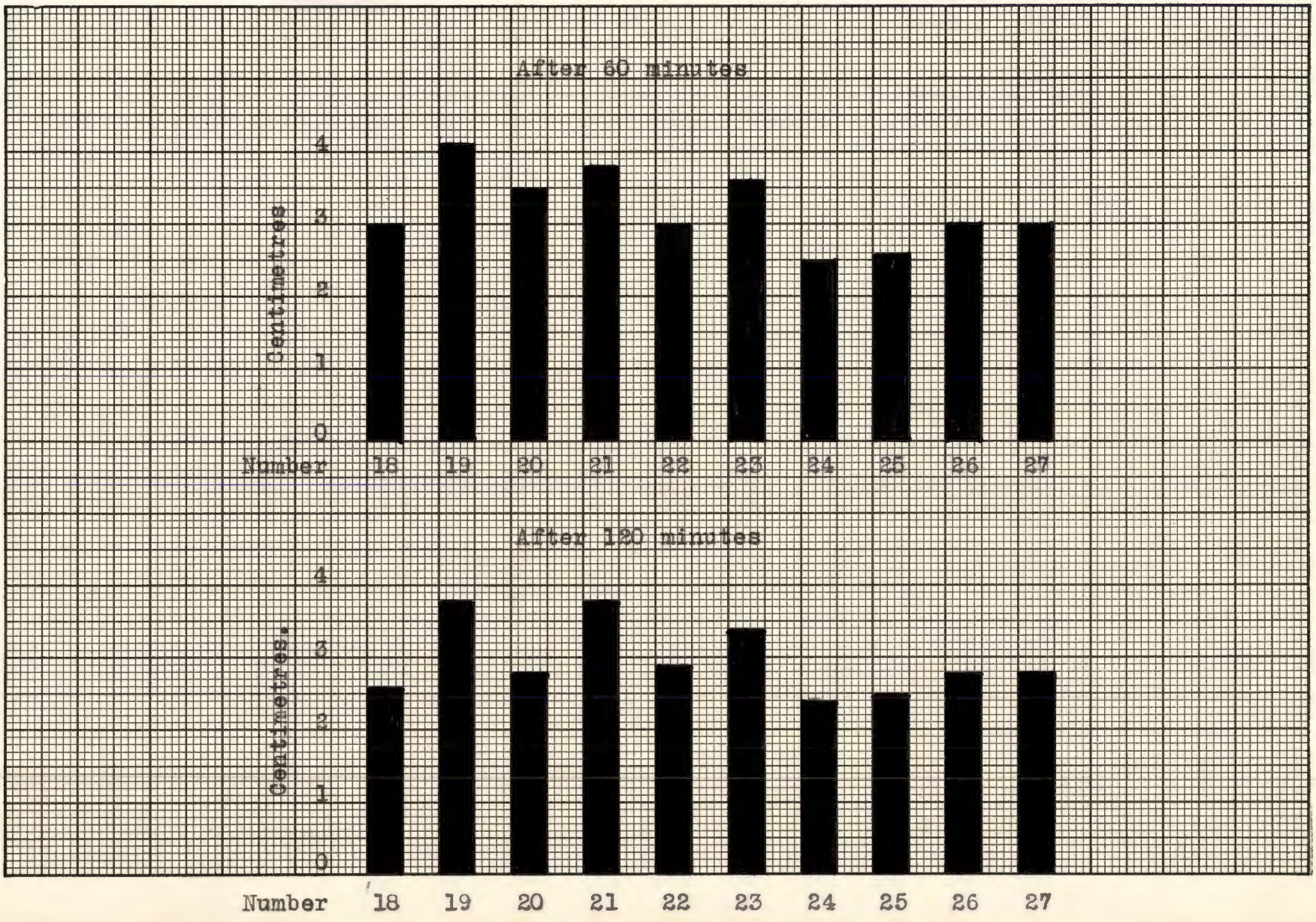
GRAPH 2 - AMOUNT OF PRECIPITATE - DRY LIME-SULPHUR SERIES.



GRAPH 2 - AMOUNT OF PRECIPITATE - DRY LIME-SULPHUR SERIES.



PRESENTATION AND DISCUSSION OF RESULTS

PHYSICAL.

Amount of Precipitate:

In the observations in the laboratory more consideration is given to the amount of precipitate or sediment than to the amount of suspended substances because with the lime sulphur and lead arsenate combination mixture a quickly settling, small amount of precipitate is desirable. This type of precipitate differs from the sort usually sought in Bordeaux mixture where the particles of precipitate while large are light in weight and hence remain in suspension for a comparatively long time. That a small amount of precipitate in the lime sulphur-arsenate of lead combination mixture is beneficial is seen by correlating the amount, with the color of precipitate, and color of solution from chemical and physical standpoints.

When only the two materials are used the least amount of precipitate at the bottom of the jars, at the end of 2 minutes, occurs when the water is added to almost the total volume, the liquid lime sulphur poured in, and finally the arsenate of lead added. However, at the end of 60 minutes the smallest amount of sediment is obtained when the liquid lime sulphur is diluted with water to almost the total volume,

and then the arsenate of lead sifted in. In both these cases it will be noticed that the liquid lime sulphur is diluted to almost the total volume with water before the arsenate of lead is added. Therefore, when a small amount of precipitate is sought the arsenate of lead should go in last to the diluted lime sulphur solution.

The greatest amount of precipitate appears when the liquid lime sulphur and arsenate of lead are each mixed to one-half the total volume with water in separate containers and then poured together through a funnel; hence, it is not advisable to have the liquid lime sulphur and arsenate of lead each made up to one-half the total volume of the tank and then pour them in together at the same time as is generally recommended as the best method of making Bordeaux mixture.

Using dry lime sulphur and cold water, the least amount of precipitate at the end of 2 minutes is seen when the lime sulphur and arsenate of lead are each mixed to one-half their total volume with water in separate containers and then poured together through a funnel. However, this is not the optimum method and it should be remarked that mixing the liquid lime sulphur in this way gives the greatest amount of sediment, but in no case is the amount of precipitate as high with the liquid as is the amount of sediment

obtained with the dry lime sulphur when other methods of mixing are used.

The greatest amount of sediment is evidenced when the dry lime sulphur is dissolved in 50 c.c. water, the lead arsenate dissolved in 50 c.c. water, the two mixed in these concentrated forms and the rest of the water added to total volume. In orchard practice this is comparable to combining the dry lime sulphur and arsenate of lead in concentrated forms, and obviously is not to be recommended.

With the liquid lime sulphur, boiling water in place of cold water reduces the amount of precipitate. The least amount of precipitate with the lime sulphur powder is secured by using boiling water and dissolving the dry lime sulphur and arsenate of lead each in one-half the total volume of water and then pouring the two in together thru a funnel. The use of boiling water, therefore, insures that the dry lime sulphur will be dissolved quicker, and thus doing away with part of the long wait necessary for the substance to enter into solution when cold water is employed.

The amount of arsenical poison in the mixture is no criterion of the efficiency of the spray solution. Amongst other factors the usual dosage of 2 pounds of arsenate of lead to 50 gallons of water does not indicate the value of the spray. The element arsenic itself is non-poisonous but

its compounds are deadly so. Lovett (40) is mentioned previously as stating that theoretically 1 pound of the acid arsenate of lead to 400 gallons of water is a sufficient dose for young caterpillars. Increased spread and adherence are also factors decreasing the amount of arsenical poison required. An even distribution of the spray material over the tree is of more importance than the amount that is merely put into the mixture. Of course on combination with the lime sulphur the arsenate of lead may be changed to a less efficient form, but a large amount of precipitate, permitting detection of the spray more easily when dispersed on the foliage, does not increase the arsenical value of the spray solution. The liquid lime sulphur studies of the amount of precipitate in connection with the color of the precipitate show that when there is a large amount it is black as a rule, the comparatively useless lead sulphide being formed; there is little advantage to be gained by increasing the amount of a useless substance. Practically all modern orchard spray machines are equipped with agitators and thus ensuring that the precipitate will be kept well in suspension. By increasing the amount of arsenate of lead added undoubtedly the control of biting insects is augmented but on the other hand the cost of spraying is increased, and arsenical injury is more liable to occur. Since the commercial

arsenates of lead are of the acid form the greater the amount added the greater will be the amount of decomposition and hence the greater the amount of precipitate. For reasons mentioned elsewhere (see page 56) a small amount of precipitate is desirable.

With the liquid lime sulphur and arsenate of lead only, then, the most desirable method of mixing from the standpoint of small amount of precipitate is to start filling the tank of the spray machine with water and at some time before it is full, preferably when about one-half full, add the liquid lime sulphur. After the tank is filled up almost to capacity the arsenate of lead dissolved in a small amount of water is poured in.

When lime is employed as a supplemental material, and it is recommended that it should be to diminish arsenical injury, it is added after the tank is almost filled with the lime sulphur solution but before the arsenate of lead is poured in, or it may be mixed in the same bucket with the latter. It is of interest to note that when lime is added before the arsenate of lead to the lime sulphur-arsenate of lead mixture in the laboratory the solution is lighter in color than when the lime is omitted; but, when lime is added in the prescribed manner to the spray tank with the engine running a moss green colored solution results. To insure

safety to the plant and at the same time make the color of solution lighter the lime should be added to the dilute lime sulphur so as to allow adequate time for the desired chemical reactions to take place. In orchard work, if it can be done conveniently, the lime sulphur-lime solution should be made to the proper dilution in the tank and the addition of the arsenate of lead be delayed as long as possible before the actual application of the spray. Soft water in place of hard gives the desired colored solution. In the orchard experiments tap water is the cause of the moss green color while water from a creek gives a light colored spray mist. There is no difference in the injury observed as none is reported in either case. However, under weather conditions more conducive to spray injury a greater difference may be witnessed in favor of the latter solution. When the spray mixture is made in the manner prescribed, opportunity is given for the excess lime to be readily available for the chemical reaction tending to convert the acid arsenate of lead to a more highly insoluble form.

The addition of the commercial caseinate to the lime sulphur solution before the arsenate of lead promotes effects much the same as lime relative to amount of precipitate, color of precipitate, and color of solution. The amount of precipitate becomes less and the color of precipitate and

color of solution lighter. Recalling that the product is two-thirds lime is sufficient explanation to account for this similarity. Different in its action than lime however, is the foaming which occurs when the caseinate is stirred in solution. This foaming is due to the casein contained in the caseinate as the usual commercial powder when mixed in water shows this property, while lime alone in water does not.

Unless proper precautions are taken certain difficulties may arise in the mixing of casein in the lime sulphur-arsenate of lead spray. By being placed in the tank before a sufficient quantity of water is added the casein substance may descend to the bottom of the container and interfere with the spreading and adhesive possibilities of the solution, by not giving optimum results; by requiring constant attention to the mechanics of the spray machine itself due to the gummy mass reducing the efficiency; and, by clogging the nozzles of the spray gun or rod. If the caseinate powder is not carefully poured through the screen into the spray tank the gummy mass will block up the meshes. Arsenate of lead sometimes gives this trouble also but to a very much less extent than the caseinate. Emphasis must be stressed on the fact that it is of the utmost importance to have the commercial caseinate powder dissolved to the state where it

will flow freely through the screen of the spray tank.

The liquid buttermilk mixes readily with the lime sulphur-arsenate of lead mixture, more so in fact than the caseinate powder. Observations in the orchard of the spreading and adhesive effects of the commercial powder and the liquid buttermilk seem to indicate that they are equally efficacious in action. The liquid buttermilk does not contain lime and hence is not as valuable as the caseinate in decreasing the possibility of arsenical injury. However, the prevention of arsenical burning must be distinguished from the increase of spread and adherence in the lime sulphur-lead arsenate spray; the two purposes are distinct from one another. It is recognized that by augmenting the spreading and adhesive powers of the solution the tendency to cause or increase injury may be promoted. (see section under injury page 96) As is shown elsewhere in this paper the addition of lime decreases the chances of arsenical injury occurring. The lime may be added to the lime sulphur before the arsenate of lead to the lime sulphur-buttermilk-arsenate of lead spray for the prevention of arsenical injury.

On the fruit and foliage the lime, caseinate, and buttermilk combination lime sulphur-arsenate of lead sprays appear as a whitish precipitate. Observations in the experimental sprayed plots show that the lime, caseinate, and

liquid buttermilk show up plainer than the usual lime sulphur-arsenate of lead on the tree after subjection to adverse weather conditions. Continued and severe rains fail to wash the supplemented solutions from the tree to the same extent as they do the common lime sulphur-arsenate of lead. The liquid buttermilk solution surely gives the best results in the tests, the lime next, and the caseinate last of the three. Since the experiment is run for only one year and but a few trees used the results are necessarily limited in extent. In view of these facts it can only be advised that further trials be run to prove the value of lime, and then one step more to the use of liquid buttermilk as a spreader.

It can be stated from the results of the orchard experiments that the spray solution containing a spreader causes the film to spread more evenly on the leaves and young apples than when no spreader is employed. To a certain extent some spreading does occur, the drops of solution tending to run together and form a continuous film.

The orchard trials do not indicate that when a spreader is used less spray solution will be required for a given number of trees; approximately the same amounts of each of the solutions are used. The chances are quite probable that the careful sprayer will keep dispersing the solution over the trees until dripping commences. Although

the same amount of solution is used the one containing the spreader gives a more uniform distribution of the film of spray solution on the fruit and foliage. Thus, while less of the solution is not employed more desirable effects are attained.

From the limited amount of work carried on the liquid buttermilk is found to be promising. Caseinate as a spreader in the Pacific coast sections is now developed to the state where it is a commercial proposition. The cost of the material is mentioned previously as one of the qualities desired in spreaders. An approximate comparison of the cost of casein in the commercial caseinate and buttermilk is as follows:

TABLE 4

COST OF CASEIN USED IN 50 GALLONS OF SPRAY SOLUTION

CASEINATE

Amount used..... 0.25 lbs.

Cost per pound.....$0.25

Cost of amount used .....25 x .25 = $0.0625.

LIQUID BUTTERMILK

Amount used..... 3.25 lbs.

Cost per pound.....$0.003

Cost of amount used.....3.25 x .003 =$0.0097.

From statistics gathered by Fogler and Thomson (23) in the regions of Wenatchee, Yakima, Idaho, Hood River, Western Colorado, and New York, the average rate of application of spray materials per day is close to 1500 gallons. Hence the use of commercial caseinate increases the cost of spraying by $1.87 per day, and the liquid buttermilk but $0.29.

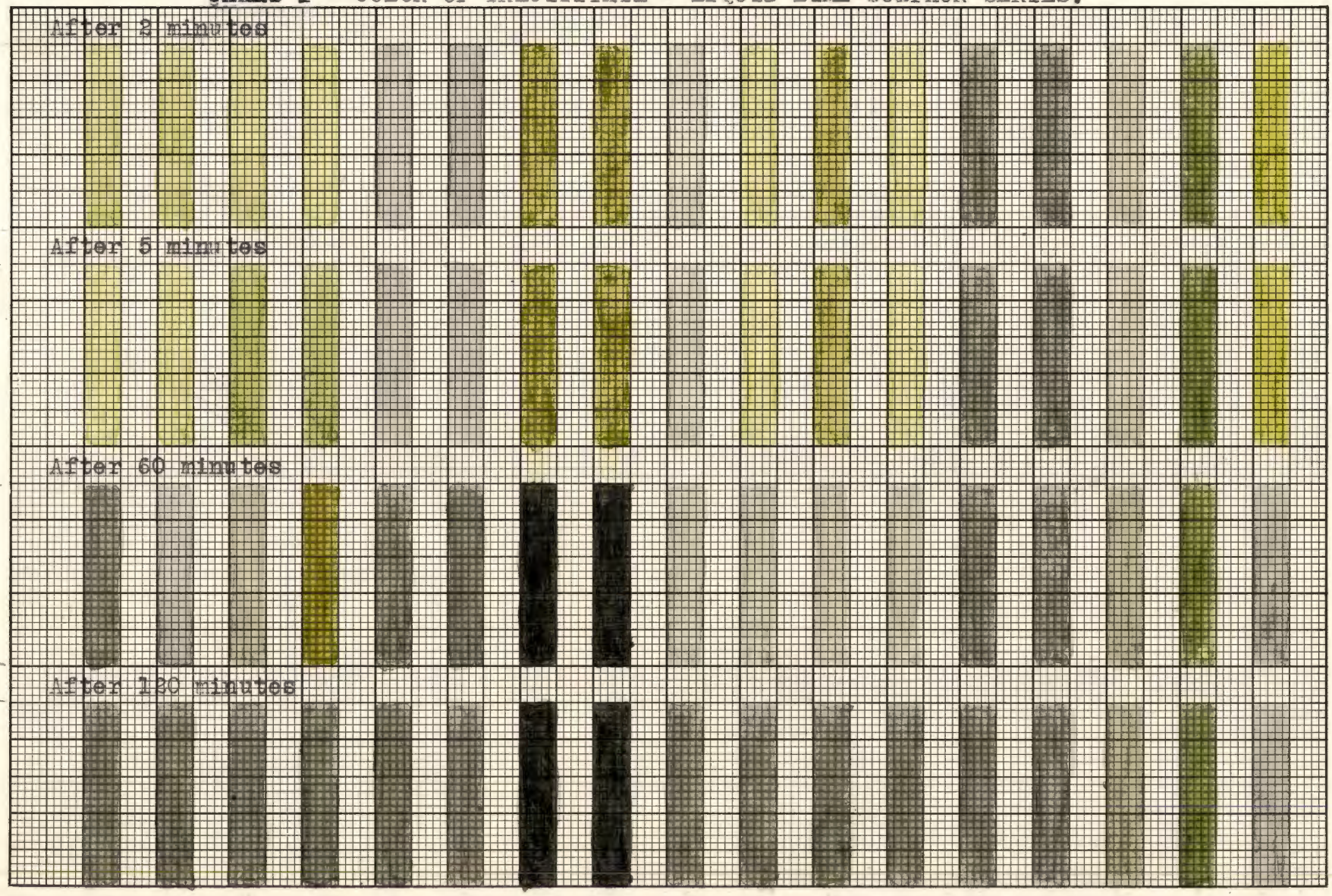
The casein-containing spreaders no doubt can be bought at a less cost than given above in large amounts, and again more gallons than 1500 are often used in a day. The values given therefore are only approximate but may be used for comparison purposes.

The question arises as to whether or not it is economically wise to increase the cost of spraying by the use of caseinate to the extent of $1.87. If it is desired to use a spreader the use of liquid buttermilk, increasing the cost per day only $0.29, from the limited work done appears to be the better proposition.

TABLE 5 - COLOR OF PRECIPITATE - LIQUID LIME SULPHUR SERIES

Mixture Number	2 min.	5 min.	60 min.	120 min.
1	Grass green	Grass green	Lead	Lead
2	"	"	"	"
3	"	Willow green	Pure gray	"
4	"	"	Pea green	"
5	Pale gray	Pale gray	Lead	"
6	"	"	"	"
7	Pea Green	Pea green	Black	Black
8	"	"	"	"
9	Silver gray	Silver gray	Silver gray	Lead
10	Grass green	Grass green	"	"
11	Pea Green	Pea Green	"	"
12	Grass green	Grass green	"	"
13	Lead	Lead	Lead	"
14	"	"	"	"
15	Pearl Gray	Pearl Gray	Pure Gray	Pure Gray
16	Moss Green	Moss Green	Moss Green	Moss Green
17	Pea Green	Pea Green	Pale Gray	Pale Gray

CHART 1 - COLOR OF PRECIPITATE - LIQUID LIME-SULPHUR SERIES.



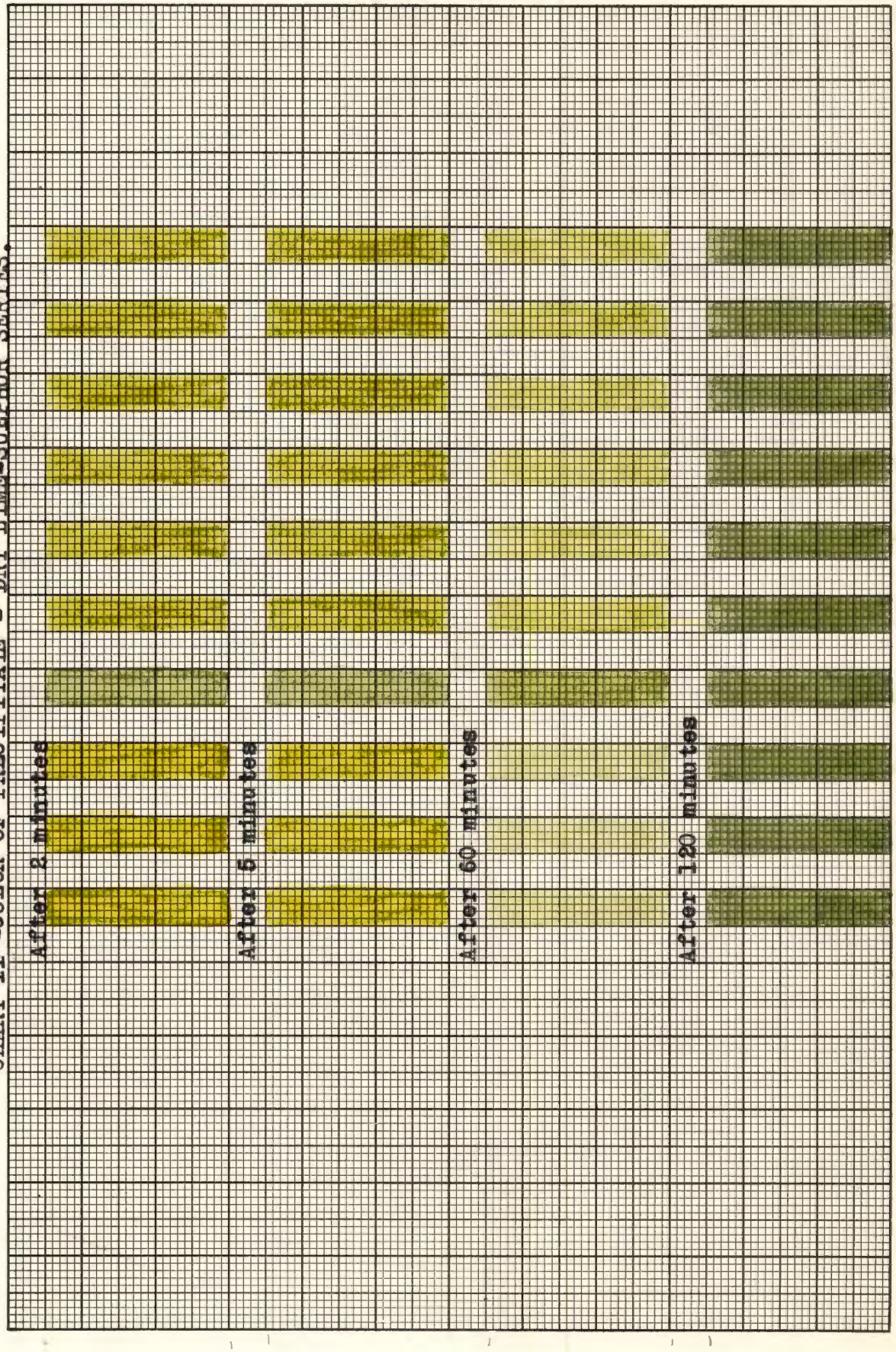
Form E-4

TABLE 6 - COLOR OF PRECIPITATE - DRY LIME SULPHUR SERIES.

Mixture Number	2 min.	5 min.	60 min.	120 min.
18	Greenish lemon	Greenish lemon	Grass Green	Moss Green
19	"	"	"	"
20	"	"	"	"
21	Willow Green	Willow Green	Willow Green	"
22	Canary Green	Canary Green	Apple Green	"
23	"	"	"	"
24	"	"	"	"
25	"	"	"	"
26	"	"	"	"
27	"	"	"	"

Form E-4

CHART 11 -COLOR OF PRECIPITATE - DRY LIME-SULPHUR SERIES.



COLOR OF PRECIPITATE.

In the historical section the information is given that when arsenate of lead is added to lime sulphur solution unless proper precautions are taken decomposition occurs and as one product a soluble product is formed. When little or no decomposition happens the sediment remains a distinct gray color; but when decomposition does take place the longer the mixture is allowed to stand the darker the precipitate becomes. As a general rule with the liquid lime sulphur the smaller the amount of sediment present the more grayish it is, being correlated with a decrease in the amount of dark precipitate taken to be lead sulphide. A dark colored precipitate may have some place in the spray solution as an indicator when applied to the foliage but in this work is considered as being undesirable.

From the standpoint of color of precipitate it is sought to secure a gray colored precipitate showing that but slight decomposition is going on and consequently a decreased likelihood of arsenical injury on application of the mixture to the trees. With the liquid lime sulphur this state is attained by pouring in the arsenate of lead after the tank has been filled with lime sulphur and water. The addition of caseinate, or lime, either lump or hydrated, will also give a gray colored precipitate. Lime and caseinate have much the same

effect when added to the dry lime sulphur-arsenate of lead solution.

Dry lime sulphur gives a very much different colored precipitate than liquid lime sulphur when mixed with arsenate of lead, the color changing in most cases from a greenish lemon shade to a moss green. Since dry lime sulphur is a comparatively new spray substance appearing on the market it is quite possible at the present time that its method of preparation is not perfect as yet and that more experimental work is required. The dry lime sulphur when mixed in water goes into solution while arsenate of lead for the most part merely goes into suspension; however, a certain proportion of the dry lime sulphur remains in suspension and a slight percentage of the arsenate of lead goes into solution. Because of these facts a certain amount of the materials will be in chemical combination, and part will be physically or mechanically mixed. This usually occurs to a greater extent with the dry than with the liquid lime sulphur, and is noticeable in the amount as well as in the color of the sediment. A color determination of the sediment therefore when the dry lime sulphur is used is not at the present time as indicative of the probability of plant injury as it is with the liquid lime sulphur. But, the addition of lime to

the dry lime sulphur-arsenate of lead solution gives in every case a lighter colored sediment and hence decreasing the possibility of arsenical injury to the tree.

By correlating the amount and color of precipitate the following reasons are advanced showing the desirability of a small amount of precipitate:

1. A small amount of precipitate because of its grayish color indicates that but slight decomposition to injurious arsenical substances, or to the comparatively useless lead sulphide has occurred.

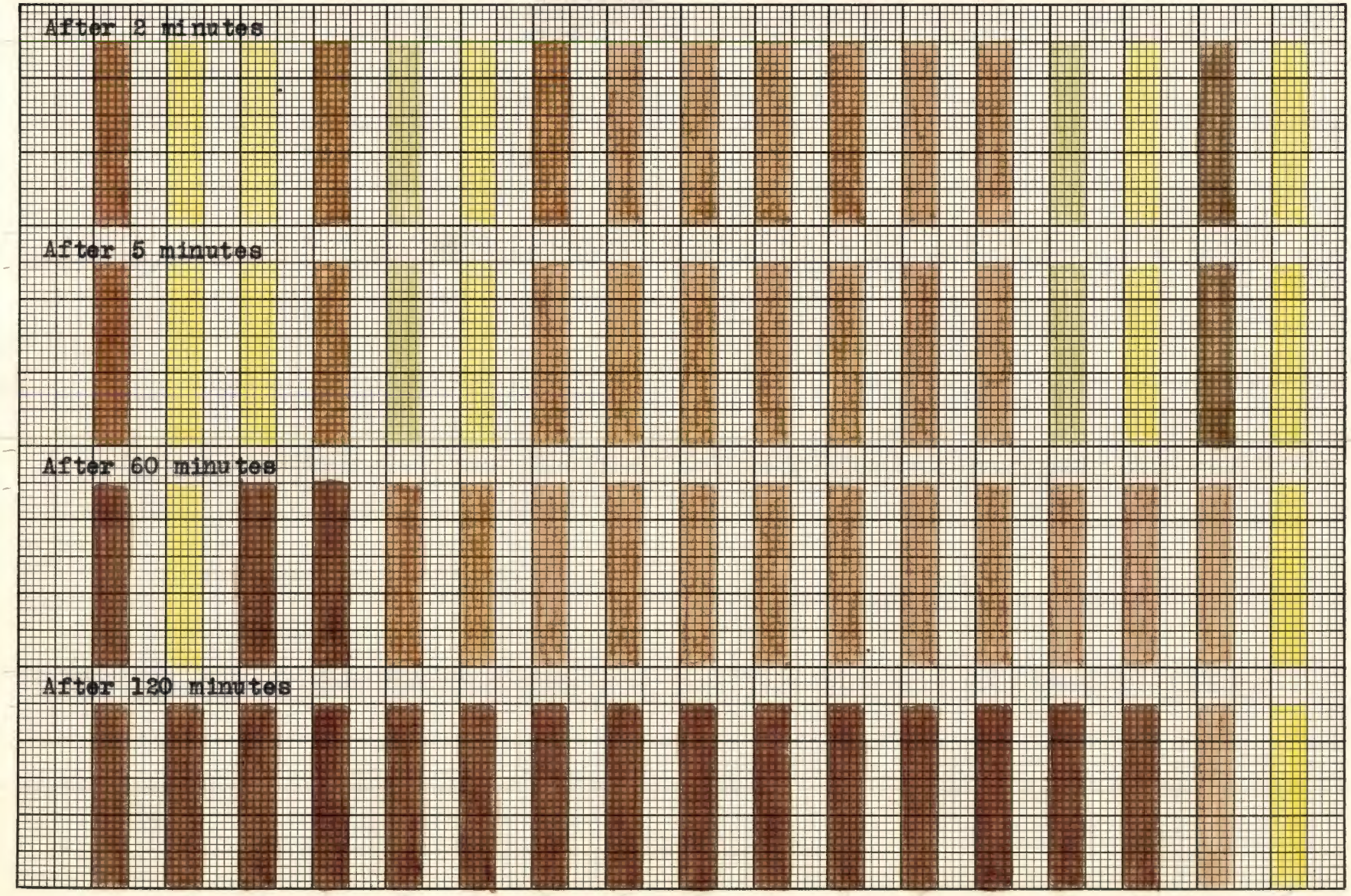
2. The use of lime as a supplemental material is shown by laboratory and orchard trials to diminish danger of arsenical injury. The amount of precipitate in this case is small and gray in color and from Robinson's (57) work there is reason to believe that relatively insoluble compounds of calcium arsenate and basic arsenate of lead are formed.

3. The employment of spreaders increases the efficiency of the spray solution and gives a small amount of precipitate when mixed in the proper manner.

TABLE 7 - COLOR OF SOLUTION - LIQUID LIME SULPHUR SERIES

Solution Number	2 min.	5 min.	60 min.	120 min.
1	Amber	Amber	Seal brown	Seal brown
2	Canary	Canary	Canary	"
3	"	"	Seal Brown	"
4	Amber	Amber	"	"
5	Grass green	Grass green	Amber	"
6	Canary	Canary	"	"
7	Amber	Amber	"	"
8	"	"	"	"
9	"	"	"	"
10	"	"	"	"
11	"	"	"	"
12	"	"	"	"
13	"	"	"	"
14	Grass green	Grass green	"	"
15	Canary	Canary	"	"
16	Morocco brown	Morocco brown	"	Amber
17	Canary	Canary	Canary	Canary

Chart 111 - COLOR OF [illegible] SOLUTION - LIQUID LIME-SULPHUR SERIES.



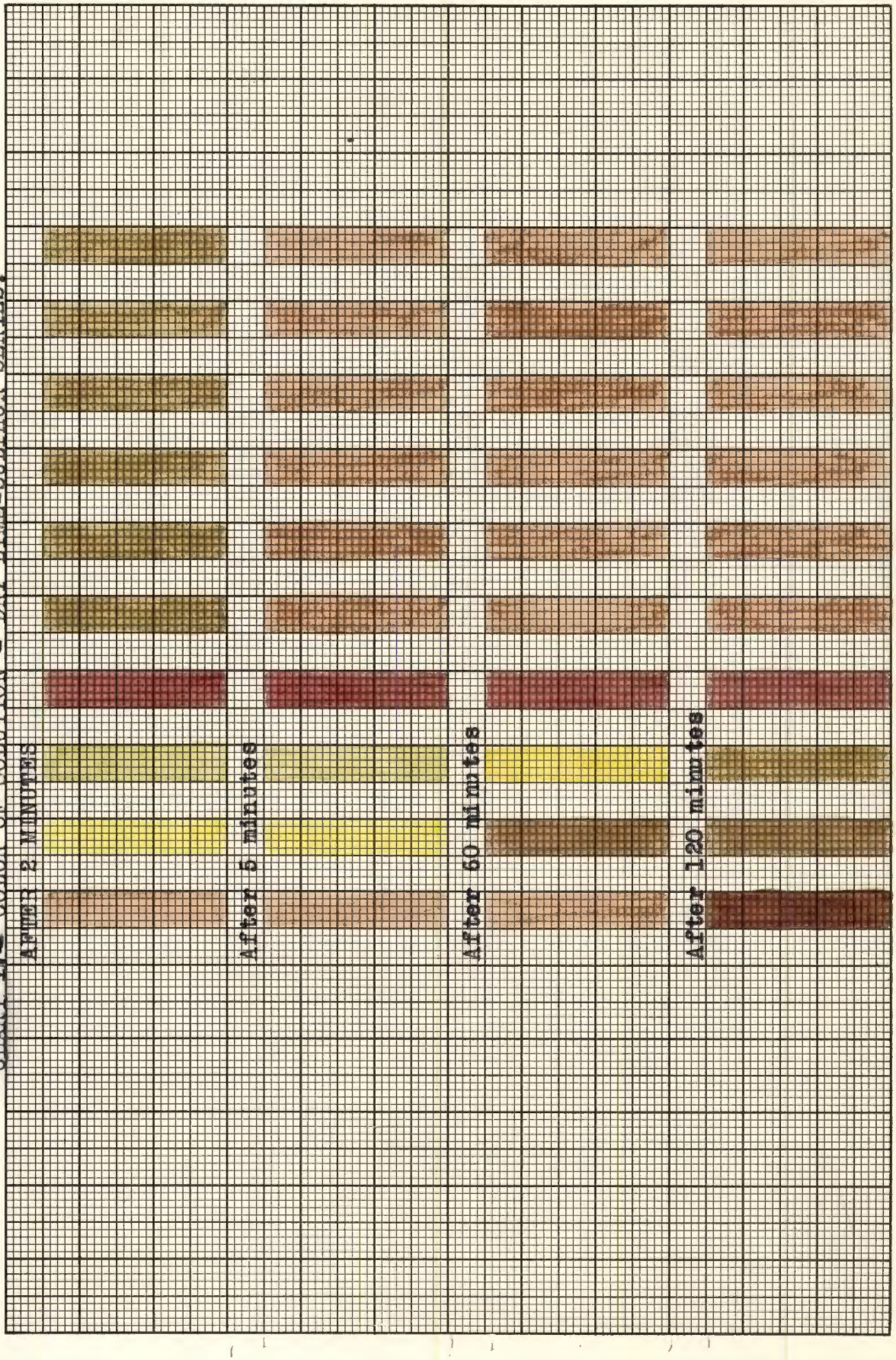
Form E-4

TABLE 8 - COLOR OF SOLUTION - DRY LIME SULPHUR SERIES

Solution Number	2 min.	5 min.	60 min.	120 min.
18	Amber	Amber	Amber	Seal Brown
19	Canary	Canary	Morocco brown	Morocco brown
20	Grass green	Grass green	Canary	Greenish Amber
21	Brick red	Brick red	Brick red	Brick red
22	Greenish amber	Amber	Amber	Amber
23	"	"	"	"
24	"	"	"	"
25	"	"	"	"
26	"	"	"	"
27	"	"	"	"

Form E-4

CHART IV- COLOR OF SOLUTION - DRY LIME-SULPHUR SERIES.



COLOR OF SOLUTION.

The color of the solution to a certain extent is indicative of the soluble polysulphide content. Within limits, Safro (61) has established the fact that the more reddish the solution is in color the higher the percentage of soluble polysulphides present. There is a certain correlation between the soluble polysulphides and the specific gravity in so far as the term "strength" may be applied to the solution. The concentrated solution of lime sulphur is almost a cherry red in color and on dilution with water becomes a lighter shade; the specific gravity also decreases on dilution of the lime sulphur with water. Concentrated lime sulphur solution is generally considered as being unsafe for spraying purposes on tree fruit foliage; it should be noted that the red color and specific gravity are comparatively high at this time.

A better understanding of the agents giving lime sulphur its peculiar properties is necessary and tests more elaborate than are attempted in this study are required before definite conclusions can be drawn at this time as to the color of solution most desirable. Dry lime sulphur under the usual conditions of mixing will generally show some shade of orange colored solution but proof is not adequate enough showing that it is safer to use on fruit

and foliage than the proportionately diluted and more reddish colored liquid lime sulphur solution.

The higher the percentage of the fungicidal agents, calcium thiosulphate, calcium sulphite, and free sulphur the lighter will be the color of the solution while these substances are in suspension. An excess of lime will also help create a light colored solution which on agitation of the precipitate will denote a small proportion of the comparatively useless lead sulphide. In application to practical orchard work, with liquid lime sulphur alone, the lighter the color of the solution the higher the dilution; while with the dry lime sulphur a light colored solution may denote either that the powdered substances are not all dissolved, or, after being dissolved are in a dilute state.

TABLE 9 - PRESENCE OF INJURIOUS ARSENICAL SUBSTANCES AS FOUND BY USING VOLCK'S AMMONIA TEST.

Solution	Reaction
Lead arsenate powder	White precipitate
Lump lime	No white precipitate
Hydrated lime	No " "
Lead arsenate plus lump lime	No " "
Lead arsenate plus hydrated lime	No " "
Caseinate	No " "
Caseinate plus lead arsenate	No " "

CHEMICAL.

Hydrogen-ion Determinations

The hydrogen-ion determinations show but slight differences in actual acidity when the substances are mixed in the different ways; the variations in the readings are so small as to be considered negligible in the present work.

Presence of Injurious Arsenical Substances

When arsenate of lead is treated in the manner outlined by Volck (75) in his "ammonia test", a white colored precipitate is formed. This white precipitate denotes the presence of an undesirable arsenical substance when present in excess quantities. When lime, either lump or hydrated, or caseinate, is added to the arsenate of lead it is found that the "ammonia test" shows a comparative freedom from white precipitate. Volck shows that:

> "Samples which show no ammonia test are practically free from foliage-injuring properties."

It appears therefore that the addition of lime to arsenate of lead greatly decreases the susceptibility to injury. It is shown previously that the addition of lime as a supplemental material prevents decomposition of the arsenate of lead spray. That is, provided the lime is added to the lime sulphur solution so as to be in excess when the arsenate of lead is poured in. Because the arsenate of lead

is slightly more soluble in alkaline than in acid solution it might appear that the lime being alkaline in nature would not prevent the dissolving of the arsenate of lead. The function of the lime is to combine with the arsenate of lead so as to give more insoluble substances and subsequently compounds non-injurious to the plant.

SUMMARY

1. There is a difference in the amount of precipitate, color of precipitate, and color of solution when the same proportions of lime sulphur and arsenate of lead are used but mixed in a variety of ways.

2. When no supplemental material is used the most desirable method of mixing with reference to freedom from arsenical injury is to almost fill the tank with dilute lime sulphur solution and then pour in the arsenate of lead powder mixed in a small amount of water.

3. Lime, either lump or hydrated, added to the dilute lime sulphur solution before the arsenate of lead, or mixed with it results in a decreased presence of arsenical substances injurious to fruit and foliage and shows a desirable grayish colored, small amount of sediment showing that but slight decomposition has taken place. The formation of the comparatively useless dark colored lead sulphide is checked. The use of caseinate leads to somewhat similar results.

4. Buttermilk, or skimmilk may be used to advantage as a spreader in the spray solution. As a source of casein they are considerably cheaper than the commercial caseinate. They do not clog the meshes of

the screen in the spray tank, a trouble often caused by the commercial caseinate powder.

5. Boiling water in place of cold (24°C) results in a decreased amount of sediment, and causes more dry lime sulphur to be dissolved in a given length of time as is indicated by the increase in redness in color of the solution.

PART II

LIME SULPHUR INJURY

It is not definitely known how lime sulphur causes injury or exerts its valuable fungicidal action when sprayed on plants. At times in the orchard the application of the solution results in an increased amount and severity of injury and in a variation in the amount of fungus diseases controlled. Various factors intimately related with the lime sulphur type of injury may be summarized under the following theories:

(a) The soluble polysulphides as the direct active agent.

(b) Absorption of the lime sulphur by the chlorophyll.

(c) Sunlight.

(d) Heat.

(e) Gas.

(f) Acid.

(g) Oxidation.

(h) Minuteness of sulphur particles.

While the soluble polysulphides through decomposition and other chemical and physical changes may cause spray injury when lime sulphur is sprayed on plants, the

fact that similar damage may occur when the soluble polysulphides are not active factors, and when the injured part is not in direct contact with the spray material is sufficient to make each theory at times independent.

HISTORICAL.

Soluble Polysulphides

That the soluble calcium polysulphides in the lime sulphur solution may be the cause of the injury is shown by Wallace (76), Safro (61), Maney and Beach (41). It may be mentioned that this theory is the one the most commonly advanced to account for injury from lime sulphur solution. When the spray solution has dried on the plant, which under conditions of low humidity and sunshine may occur in ten minutes time, the substances causing injury are said to be decomposition or oxidation products of the soluble polysulphides.

Absorption of the Lime sulphur by the Chlorophyll

Under certain conditions of sunlight Sanders (64) finds by sectioning leaves injured by lime sulphur, and putting them under the microscope that the lime sulphur is absorbed by the leaves, causing a marked change and browning of the chlorophyll in the palisade tissues.

Sunlight

The ultra-violet rays, as well as the lime sulphur may also be absorbed by the chlorophyll in the leaves and cause injury, as is pointed out by Palladin and Giubbenet (52). But there is a difference in the extent to which different types of leaves will absorb the actinic rays. In this connection Dangeard (19) mentions that hairy leaves retard penetration of the violet and ultra-violet rays through the tissues more than glaucous or smooth ones.

The thickness of the epidermis is also of interest in relation to spray injury under the influence of the actinic rays of the sun. Maquenne and Demoussy (42) call attention to the fact that leaves are often blackened under the influence of electric light. When leaves with a thin epidermis are exposed by them to the action of a mercury lamp, the light of which is very rich in ultra-violet rays, the leaves are blackened within two to three hours, while if the epidermis is rather thick it requires ten to twelve hours to produce such an effect. Their work indicates that the action of the ultra-violet rays results in the destruction of the protoplasm of the cells of the plants. The experiments lead them to the belief that the action is a diastatic one and is generally due to the effect produced on the oxidase following the destruction of the protoplasm.

Now it may seem a paradox that by sunlight there shall be injury caused to the green coloring matter of the leaves. We expect in sunlight to have a building up of tissue and organic material due to photosynthesis. In this case, which is the usual occurrence, the longer rays of the spectrum are exerting more influence than the actinic rays; the action of the shorter rays being negligible.

In this connection Wiesner (77) may be quoted as follows: "Light not only aids in the development of chlorophyll but at higher intensities brings about its destruction probably through oxidation. The decomposition of chlorophyll occurs outside the plant as well as within its tissues. This can be demonstrated by exposing a test tube containing a solution of chlorophyll to the light and comparing it with others kept in darkness. Red and yellow light are most effective in destroying chlorophyll."

Two primary factors of interest here are given by Garner and Allard (26) as entering into the action of light upon plants, viz., (a) the intensity of the light, and (b) the wave length. As regards intensity they state:

> "Within limits, reduction in light intensity tends to lengthen the main axis and branches and to increase the superficial area of the foliage of many species. Also, the thickness of the leaf lamina may be reduced, and there may be marked departures from the normal in internal structure, the tendency being toward a less compact structure."

In its relation to spray injury this statement is of particular interest especially if such conditions are present at a time when there is a depletion of the chlorophyll

content of the leaves as Sanders (64) in his studies on the effect of light on the chlorophyll content mentions that plants kept for a period in darkness and then exposed to sunlight show a burned appearance more readily than those kept in full sunlight. The explanation offered by him is that chlorophyll is not manufactured in the absence of sunlight, and the depletion of chlorophyll following a period of darkness results in more serious injury when the leaves are again exposed to sunlight.

This viewpoint is strengthened by the investigations of Bonnier (9) who using one-third the intensity of sunlight by employing electric light, observes a lessening in amount of chlorophyll formed even to unusual depths.

Hence when we have conditions bringing about a depletion of the chlorophyll content of the leaves, the foliage becomes more susceptible to spray injury on exposure to sunlight. Darkness thus is one of the factors influencing this phenomenon.

In connection with the factors mentioned previously, (thickness of epidermis, pubescence, and looseness of internal structure) the work of Gourley and Nightingale (27) is of value in showing the effects of shade on plants. In their work on the effect of shade on foliage and structure of leaves they state:

"Not only was the area of the leaf surface affected to a marked extent by the shading, but the contour of the surface was also strikingly changed. This was particularly true with the peach, the leaf of which is normally somewhat wrinkled, the edges upturned so as to make the leaf decidedly concave, and the midrib is usually reflexed. In contrast to the usual appearance of the leaf, those in the shade were much flattened as to their surface, but somewhat drooping and limp, glabrous, and of a much intense green color. This latter condition would appear to be due to an accumulation of nitrogenous substances and a comparative reduction in carbo-hydrates.

Just as the outward appearance of the leaves were affected by their treatment, so the internal structure was also modified. One of the outstanding differences between the treated and untreated ones was in thickness, which was common to all the plants under observation.

The structure of the apple leaf is usually characterized by at least two layers of palisade cells, and often by a third one; the mesophyll is rather dense and the epidermis is relatively thick. In contrast to this condition the shaded leaves possessed but one layer of palisade cells (occasionally a second layer of shorter cells), the mesophyll was loose in structure, and the epidermis was thinner than that of those grown in direct sunlight. The "sun" leaves were on the average 90 percent thicker than those grown in the shade.

The peach leaves were similarly affected but to a less extent than those of the apple. The "sun" leaves examined were on the average 20 percent thicker than the "shade" ones. They also possessed a thinner cuticle and epidermis on the upper surface but no measurable difference was apparent on the underside. As in the apple, the peach leaves showed a decided modification in the palisade tissue. The "sun" leaves possessed three layers of palisade cells as compared with the "shade" ones, which had two layers or only one. Also the division point between the spongy mesophyll and the palisade area was very distinct in the "sun" leaves, while in the "shade" ones no definite dividing line could usually be distinguished, owing to the loose arrangement and irregular shape of the second layer

of palisade cells. The whole structure of the "shade" leaves was loose, while that of the "sun" leaves was relatively very compact, and the cell walls thicker, particularly near the upper surface."

It is well known that when lime sulphur is sprayed on the fruit of the apple on hot, sunshiny days injury is liable to appear. Caesar (11, 12) is of the opinion that sun-scalding of certain varieties after spraying with lime sulphur on a hot, calm, sunny day on the sun exposed parts will show the injury after the fruit has got to be one-half inch, and up to two inches in diameter. Shaded fruits are not at all affected even on the same tree. Safro (61) states that,

"Cases reported as lime sulphur injury are frequently due to other causes, often sunburn."

The following extract from his work supports the above statement: "The following items lead to the belief that if lime sulphur causes the injury it is not the sole cause, or at least there were modifying factors.

1. The injury was by no means general in its distribution throughout the plot; it was almost exclusively restricted to the southwest corner of the tree.

2. The injury was far more common on low-hanging, almost horizontal branches than higher up on the tree or upon upright branches.

The restriction of the area of injury to the southwest corner of the tree suggested the sun as a factor in the occurrence of the injury.

During the hottest part of the day the sun is in the southwest and the heat given off by the sun to the southwest corner of the tree is much greater than the heat given off to any other part of the tree. The following items tended

to strengthen the possibility of the sun being a direct factor in the production of the injury:

1. Injury was found only upon apples exposed to the direct rays of the afternoon sun. Apples shaded by leaves or branches showed no injury.

2. On the individual apple, the injury occurred only upon that part exposed to the direct rays of the afternoon sun. Only the part of the apple that had sufficient sunlight to begin taking on color was injured, no injury being found upon entirely green apples or upon the green portion of partly colored apples.

In consideration of these items that status of the cause of the injury seemed to be that the lime sulphur as used was non-injurious under ordinary circumstances but that under the direct rays of the sun during the hottest part of the day the spray upon the trees was rendered injurious."

In propounding his theory on the dropping of apples sprayed with lime sulphur Sanders (65) writes as follows:

"From such information as could be gathered from other sections, and from varying experiences in different seasons, it was found that the intensity of the injury seemed to vary with the amount of sunlight during May, June, and July. In England, New Zealand, and Kootenay Valleys in British Columbia and in Nova Scotia fruit removal by lime sulphur seems to occur every year. - In areas such as Ontario, New York State, New England, etc., where there is more sunlight, say an average of over 250 hours of sunshine permonth during May, June and July, it would seem that serious fruit removal by lime sulphur only occurs in seasons when the amount of sunshine per month drops below that figure. Since chlorophyll depends on sunlight, not only for its action in converting carbon dioxide into sugar but for its own actual formation, it can readily be seen that in years of

> plenty of sunlight the chlorophyll would be replaced almost as fast as it was injured and the injurious effects on the crops and tree rendered almost negligible. Whereas, in years of little sunlight the injury might be severe in the same areas."

The experiments of Flammarion (22) while performed for a separate purpose may be applied to the subject under discussion. In his investigations he carries on trials in houses of colored glass constructed so as to permit the control of exposure to the desired color and length of light ray. He is concerned with the effect of red, green, and blue rays on the growth of plants and shows that plants under blue glass make very inferior growth to the ones under the influence of the red and green rays. He finds that geranium leaves lose their reddish-brown tone and change under the red, blue, and green rays into the three following forms: in the red glasshouse they are large, well cut, and pale green; in the blue almost round and dark green; and in the green small and very pale green. The same results are produced with peaches, apples, cherries, and strawberries. The geranium leaves subjected by him to full radiation show a brownish coloration about the zonal section. In the Coleus leaves it seems that very dim light, and green, and blue rays have similar effects on the coloration. His work illustrates that the various rays of the spectrum have different influences on foliage and tend to

approach the effects perceived in the orchard after spraying and/to which the blame is often solely laid to the spray material.

Heat

It is shown by Money and Beach (41) that the presence of the actinic rays of the sun and a temperature of 102° F. are necessary for spray injury to foliage from lime sulphur solution. They also find that when the actinic rays are not exerting an influence a higher temperature is necessary before injury to the leaves will result, and obtain this effect in the absence of the sun's rays by placing leaf-bearing twigs of apple covered with a film of spray solution in the electric oven at a temperature of 108° F.

From his experience with dusting materials Sanders (65) states: "It must be remembered that the copper dust is a better fungicide than sulphur and that there is danger of any sulphur compound burning the fruit and foliage if the temperature remains above 95°F for any considerable period following its application."

The opinion of Barss (6) indicates the need for definite information on heat as a factor in lime sulphur spray injury. He writes as follows:

> "Temperature has an important effect on the activity of sulphur sprays. In hot weather, weaker dilutions of lime sulphur should be used. No accurate experiments have yet been conducted to determine the exact relations of temperature to sulphur sprays, but the Crop Protection Institute, is, I understand, about to undertake such studies during the coming season. These should give us some very valuable information which has long been needed. It is to be hoped that in these investigations efforts will be made to determine how spray injury may be avoided under all circumstances. Meanwhile the grower must follow with care such practices as will keep his trees in the most vigorous condition possible, applying the early protective sprays faithfully and using greater dilutions in hot weather."

The observations of Barss (6) also indicate that the so-called "sulphur-shock" which occurs when for some reason the earlier lime sulphur applications are omitted is likely to be influenced and brought about by a high temperature, or at least during the season of the year when high temperatures are usually prevalent.

Gas, Acid, and Oxidation

The theories concerned with gases, acids, and oxidation are closely related. In this connection the general occurrence would be for a gas to be set free from the lime sulphur solution or from decomposition of the solution. The gas then would undergo a change resulting in the formation of an acid. It may be that from lime sulphur the acid would be sulphuric. The brown coloration of the injured part would be the outcome of oxidation.

Observations of the action of sulphur powder in the greenhouse lead to the belief that when sulphur (S) is left on the pipes heat and sunlight under certain conditions liberate an appreciable amount of gas. In support of this view Norton and White (52) point out that vaporizing sulphur without ignition, as by painting it on the heating pipes or warming it over lamps, is usually effective in controlling the mildew of roses.

From their experiments on the germination of fungus spores Barker, Gimingham, and Wiltshire (5) conclude that none of the compounds such as hydrogen sulphide, sulphur dioxide, sulphuric acid, hydrogen peroxide, caustic soda, ferrous hydroxide, and calcium sulphate, which may possibly be derived from sulphur will account for its toxic action. They believe moreover that the trace of sulphur which is soluble in water is not sufficient to act fungicidally and find that conidia and spores of Sclerotinia fructigena will germinate in sulphur washings and hanging drops. While they believe that a gas is partly responsible for the toxic effect of the fungicide they are unable to show definitely the presence of it in sufficient amounts.

Very little sulphur dioxide (SO_2) will be formed by the direct union of the oxygen of the air and the free sulphur deposited on the leaves from reduction of the sulphur

containing compounds under ordinary conditions. Although SO_2 can be formed by burning sulphur in air or oxygen, a temperature of about 250-260° is given by Thorpe (73) as being required for ignition. It seems therefore that the possibility of the formation of SO_2 from the elements O_2 of the air and S set free from the lime sulphur will be very remote.

Another possible source whence SO_2 may be derived is stated by Thorpe, who mentions that SO_2 may be formed by simply oxidizing a sulphide. Since sulphides form the major portion of the lime sulphur the possibility of the formation of SO_2 from this source is self-evident.

It is claimed by Shafter (68) however, that SO_2 is not formed in appreciable amounts from sulphur deposited by lime sulphur except at temperatures much above those found under spraying conditions in the orchard. He believes that the liberation of this gas is not in amounts large enough to make it of any importance in any consideration of the insecticidal properties of the spray.

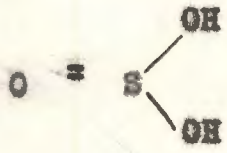
Certain weather conditions, i. e., sunlight and moisture, facilitate the union of the S and O and the rapidity with which the product of the reaction is changed. Since the maximum valency of sulphur is six, SO_2, in which but four of the valences of sulphur are used, is unsaturated

and is, therefore, still able to combine directly with suitable elements.

SO_2 dissolves readily in water yielding sulphurous acid, H_2SO_3 -

$$SO_2 + H_2O = H_2SO_3.$$

Caven and Lander (13) elucidate, in considering the structure of sulphurous acid and its salts, that two possibilities are presented; the acid may be formulated:



Symmetrical H_2SO_3

or

Unsymmetrical H_2SO_3.

They point out that such dual structures are theoretically possible in all cases where the nuclear atom is incompletely oxidized, and it is to be supposed that the stability of the unsymmetrical form will depend on the oxidizability of this atom.

Sulphurous acid is a strong reducing agent combining readily with oxygen, either free or combined, to form sulphuric acid -

$$H_2SO_3 + O = H_2SO_4.$$

Molinari (48) remarks: "The acid is not known in the free state, but is supposed to exist in aqueous

solutions obtained by saturating water with SO_2. With time, and in the light, the solution decomposes with separation of sulphur and formation of sulphuric acid."

When a solution of sulphurous acid is allowed to stand in contact with air, it slowly absorbs oxygen and unites with it to form sulphuric acid, in solution -

$$2\ H_2SO_3 + O_2 = 2\ H_2SO_4.$$

Sulphuric acid has also been obtained recently (1910) by the action of ultra-violet rays on moist SO_2, as is shown by Molinari (48).

Pollacci (53) finds that a paste of S and water is oxidized by the air at 25-30° C. to H_2SO_4. The action is accelerated by (a) - movement of the air, and (b) - sunlight. A paste kept in an atmosphere of H is not oxidized; from this the author concludes that the oxidizing action is not due to decomposition by the water. He attempts to show that the action is to be ascribed to ozone rather than to the O_2 of the air. From a study of the oxidation of the sulphides the author forms the opinion: (1) All the sulphides are oxidized by the air even below 30° C. (2) The action is accelerated by sunlight, movement of air, and above all by fine pulverization. (3) O is not fixed to form sulphates. (4) The S thus set free is oxidized to H_2SO_4 which reacts to form sulphates.

The following reasons are given by Haywood (29) against the theory that the injury is due to the sulphur dioxide or sulphurous acid:

> "(1) If the action were at all considerable we would expect that the total sulphur on the tree would decrease, since not all would be likely to be absorbed by the calcium hydroxide or calcium carbonate present, these being only mechanically mixed with the sulphur. In our experiments (which to be sure are artificial), no loss of sulphur was shown after four weeks.
>
> (2) We would expect the free sulphur to decrease during the course of four weeks: instead of this it increases to a slightly greater extent than corresponds to the amount of thiosulphate broken up according to the following equation, $CaS_2O_3 = CaSO_3 + S$."

> On the other hand Haywood quoting Pough says, "He believes that the action of the wash is to be attributed to the gradual oxidation of the sulphur which gives rise to sulphur dioxide or sulphurous acid when moisture is present, and that it is these constituents that do the work. In support of this theory he cites cases where an odor resembling sulphur dioxide is plainly discernible on hot, sunny days in the vicinity of orchards sprayed with lime sulphur."

It is well known that pure sublimed sulphur contains small amounts of sulphuric acid. When sulphur is gently heated over steam pipes Kraemer (35) shows that it gives off sulphuric acid. Pure sublimed sulphur is found by Marcille (43) to contain from 0.2-0.625 percent anhydrous sulphuric acid.

Claiming that experiments have not been carefully conducted in determining the manner in which sulphur acts

as a fungicide Marcille carries on some tests in Tunis to settle this point. It is generally asserted that the sulphur acts through its volatilisation or oxidation, but the author finds that, under the conditions of his experiments, these two functions are of very little importance. He insists that the sulphur used for the powdery mildew of roses owes its efficiency to the sulphuric acid that it contains. The efficiency of sulphur as a fungicide is believed by Kraemer to be due to the sulphuric acid, and he shows that a solution of 1 part of sulphuric acid to 1000 parts water when employed as a fungicide for mildew of roses will control the disease and leave the plant uninjured. For the control of the Black Rot of Grape Prunet (54) recommends spraying with a solution of sulphuric acid up until the time when bloom appears. Sulphuric acid in 5-10 percent solutions is applied by Rabate (55) and Hilier (31) for the eradication of weeds in cultivated fields with good results; the weeds being destroyed and the grain (wheat) uninjured. The selective action is supposed to be due to the greater moisture content of the weeds.

Maney (41) after spraying apples with sulphuric acid 1-1000, obtains injury similar to sun-scalding from

lime sulphur by exposing the apples on a window sill to the direct rays of the sun.

A suspension of finely ground sulphur in water is used by Morse (50) at the rate of 10 pounds to 50 gallons for the control of apple scab. While scab did not develop sufficiently in the orchards during his experiments to make the test a severe one it is evident from his results that sulphur used in the manner described has considerable fungicidal value. As compared with the check his percentage of scabby apples is reduced from 12.5 percent to a little over 3 percent in 1914, and the figures corresponding in 1915 are 9 percent and 0.5 percent.

The experiments of Blodgett (8) are so closely connected with the problem at hand that it seems expedient to quote an extract from his results;

> "Since there was reason to believe that the fungicidal value of lime sulphur is due in part to the fine sulphur deposited on the leaves, it was thought that it would be possible to approximate the results obtained with lime sulphur solution by applying finely ground sulphur instead and thus to avoid the burning of tender foliage. Experiments were, therefore, carried out with a mixture of sulphur and arsenate of lead applied as a liquid spray in comparison with regular lime sulphur applications for the control of apple scab. The dustings with sulphur and sulphur in suspension in water controlled scab to a very large extent closely approximating that of lime sulphur solution. The control of insects was best on the dusted plat and the apples from this block graded best commercially."

Lodemann (39) and Bailey (1) give formulae with sulphuric acid as a substance employed with iron sulphate and water solution. No mention is made in their publications of any direct value derived from the sulphuric acid itself, the purpose of the acid evidently being to accelerate the action of the iron sulphate.

METHODS OF EXPERIMENTATION

INFLUENCE ON CHLOROPHYLL.

Leaves

In investigating the causal influences of lime sulphur injury, apple foliage not being available, zonal geranium leaves are used. The leaves are cut from greenhouse plants and thoroughly sprayed with concentrated lime sulphur solution. Leaves are also taken but not subjected to the lime sulphur so as to furnish the check. A set of leaves sprayed with the lime sulphur and the check are exposed for ten minutes time at a distance of six inches from the Cooper-Hewitt quartz arc lamp. The leaves treated with the lime sulphur and exposed to the actinic rays are washed with distilled water to remove the traces of precipitated sulphur and other like foreign material.

Chlorophyll Extract

Chlorophyll is extracted from geranium leaves by boiling the foliage in water for ten minutes and then immersing in wood alcohol for 24 hours. Combinations are made in test tubes of chlorophyll, wood alcohol, hydrogen peroxide, and liquid lime sulphur. The resulting physical appearance of the mixtures is noted.

Alcoholic extract of chlorophyll of geranium foliage one-half inch in depth is placed in a petri dish and

exposed to the influence of the actinic rays of the quartz arc lamp.

Gases

The standard potassium iodate-starch, and lead acetate tests are made for the presence of sulphur dioxide, and hydrogen sulphide gases. The liquid lime sulphur is poured into beakers placed in a moist chamber and covered with filter papers soaked in the indicator solutions. The filter papers are not allowed to come into contact with the lime sulphur. 5 c.c. of the solutions of the indicators are poured into test tubes and connected by a delivery tube to an Erlenmeyer flask containing liquid lime sulphur.

The effects of the gases on apple foliage is tested by placing leaves over beakers in a similar manner as the moist filter papers in the test for the presence of sulphur dioxide and hydrogen sulphide.

Elm bark covered with Pleurococcus is stripped from the tree and suspended by a needle thrust through the cork in Erlenmeyer flasks containing liquid lime sulphur, flowers of sulphur, and distilled water. The solutions are not allowed to come into direct contact with the algae.

Anyone who has ever worked with lime sulphur will be aware of the penetrating and lasting effects of the odor

given off. To determine the effects of the substances liberated from lime sulphur the liquid material is poured into an Erlenmeyer flask, boiled, and distilled. The distillate is permitted to run into a test tube. A further connection is set up consisting of another test tube arranged to catch any substances given off from the first test tube. In another instance, liquid lime sulphur is allowed to stand in an Erlenmeyer flask with is connected by a delivery tube to a test tube containing a small amount of distilled water. In a like manner test tubes containing algae are set up in order to observe the influence of the substances seen to be passed over on these lower forms.

Microscopical examinations are also made of the appearance of the crystals of the substances which appear in the distillate of the boiled lime sulphur solution, and in the distilled water solution of the unboiled lime sulphur solution. Aqueous solutions of unboiled and boiled flowers of sulphur are employed as the check.

When sulphur dioxide and hydrogen sulphide combine with water it was thought that sulphurous or sulphuric acid might be formed. To test this possibility acidity trials are run with Congo Red solution, litmus paper, phenolphthalein, and by connecting solutions of 5 c.c. of blue litmus pater solution in test tubes connected by a delivery

tube to the Erlenmeyer flask of liquid lime sulphur as in the detection tests for sulphur dioxide and hydrogen sulphide.

Microchemical tests with barium chloride are made of the apple leaves found to be injured when placed over the lime sulphur for the presence of sulphates. Apple leaves injured by the orchard spray of lime sulphur and arsenate of lead are similarly tested.

Sulphuric Acid

In attempting to determine the presence and amount of sulphuric that might be formed or liberated externally to the plant from lime sulphur, recourse is made in one instance to the employment of glass slides. Lime sulphur (concentrated), lime sulphur (1-40), lime sulphur mixed with arsenate of lead, dry lime sulphur, and water as a check are sprayed in triplicate upon the roughened surface of 7 x 2½ centimeter slides. Some of these slides are placed in an oven at 105°F., others in a dark room, on a window sill, and on a side bench in the greenhouse. Filter papers soaked with the solutions are also subjected to the same conditions. After one week's time the material is washed off the glass slides and filter papers with 25 c.c. water and tests made for the presence of sulphuric acid, as follows:

(a) With litmus paper

(b) By precipitating with $BaCl_2$ and weighing as $BaSO_4$ in the usual way.

(c) With thesulphur-photometer

(d) With the electro-metric hydrogen-ion apparatus.

To ascertain the possibility of the formation or liberation of sulphuric acid under the influence of the actinic rays liquid lime sulphur solution is poured into a petri dish and exposed at a distance of six inches from the Cooper-Hewitt quartz arc lamp which furnishes actinic rays. The solution, one-fourth inch in depth, is stirred constantly to facilitate penetration of the actinic rays. After exposure for one-half hour the solution is tested with litmus paper and with the hydrogen-ion apparatus.

The presence of sulphuric acid in an aqueous solution of flowers of sulphur is tested by dissolving 5 grams of the sulphur in 100 c.c. of water, and after stirring at intervals for one-half hour a strip of blue litmus paper is dropped in. An acidity test is also made with Congo Red solution.

The effect of sulphuric acid on the fruit and foliage of the apple is tried under orchard conditions. Plot 4 of Orchard E as previously diagrammed is sprayed as follows:

Water	50 gallons
Sulphuric acid	½ pint

The water is pumped into the tank and the sulphuric acid added when about one-half full. The above proportions give a dilution of 1 part of the acid to 1000 of water.

PRESENTATION AND DISCUSSION OF RESULTS

INFLUENCE ON CHLOROPHYLL

Leaves

TABLE 10 - INFLUENCE OF ACTINIC RAYS ON LEAVES SPRAYED WITH LIME SULPHUR

	Treatment of Leaves	Appearance
1.	Sprayed with lime sulphur and exposed to actinic rays	Indications of bleaching
2.	Sprayed with lime sulphur but not exposed to actinic rays	No change
3.	Exposed to actinic rays but not sprayed	No change

It will be observed from the above table that the actinic rays possess the power of causing a bleaching effect on geranium leaves. If heat 100-110° F. is applied at the same time a brownish coloration will result. Since the leaves exposed to the actinic rays but not sprayed with lime sulphur solution do not show any change it seems that lime sulphur in some way is necessary for the effects perceived.

However, an apparent bleaching is observed in apple leaves in the greenhouse which are not sprayed with

lime sulphur. This phenomenon is brought about by a burning due to a concentration of the sunlight by the glass. It is noted that the injury shows as a whitish coloration; the spotting being brown in the centre or focused part while the fringe is whitish. Attention should be drawn here to the fact that in the experiment with the quarts arc lamp it is found that the presence of lime sulphur on the leaves is necessary for the bleaching effect, while in the greenhouse the bleaching occurs about the brown centre on leaves which have not been sprayed with lime sulphur solution. The point of interest is that in one place the actinic rays alone, in another the actinic rays plus lime sulphur, and both are influences bringing about the bleached and subsequent brown coloration in green leaves.

Chlorophyll Extract

In the following table the substances combined and the influences subjected to are marked with an (x).

N. B. - In this table the numbers refer to a series of solutions mixed in test tubes for observation and not as in Part I as an index to the methods of mixing.

TABLE 11 - COLOR CHANGES IN CHLOROPHYLL EXTRACT SOLUTION UNDER VARIOUS COMBINATIONS AND INFLUENCES

Number	Extracted Chlorophyll	Alcohol	Hydrogen peroxide	Liquid Lime-Sul.	Actinic Rays	Electric Current	Heat	Resulting Color Change
1		x	x					No Change
2		x		x				No Change
3	x		x					Green to White
4	x			x				Green to Dark Brown
5			x	x				Amber to Cream
6		x	x	x				Amber to Cream: Brisk Reaction
7	x				x			Green to White
8	x				x		x	Green to Brown
9	x						x	No Change
10		x				x		No Change
11	x					x		Green to Brown

From the foregoing table it is seen that the bleaching and browning effects witnessed in leaves may be due in part to oxidation. That oxidation does take place is proved by passing the electric current through the water diluted, alcoholic chlorophyll extract. At the pole where nascent oxygen is liberated the chlorophyll is oxidised and given off in flakes from the wire. In addition a marked browning of the solution occurs. No evidence of brown coloration is perceptible when water diluted alcohol is used alone, showing that the presence of this substance does not influence the oxidation of the chlorophyll.

Observations lead to the impression that the factors conducive to injury of this nature are high pressure, forcibly driven, coarse sprays, conditions leading to a thin epidermis, reduction of pubescence, loose internal structure, presence of nascent oxygen, strong sunlight liberating actinic rays and heat, and subsequent final killing and oxidation of the tissues. It will be seen from this that spray injury is correlated to a great extent with weather conditions.

Gases

A microscopical examination of leaves injured by the cluster bud spray of lime sulphur and arsenate of lead shows that the affectation first appears on the underside

of the leaf as a slight russetting. The injurious substance evidently enters through the stomata as the browning begins at these openings. Within 24 hours the brown coloration works through the leaf to the upper surface.

It was stated previously that the addition of a spreader may tend to increase the spray injury. The idea has been expressed that there is the possibility of the change in the surface tension affording a means of more of the injurious substances entering the stomata. The lowering of the surface tension and the increased area covered with the thin film are two of the factors concerned. In the cluster bud spray some injury is noted in all the plots sprayed. The browning of the leaves occurs mostly in the lower parts of the tree where the spray gun has been held close to the foliage. The under surface of the apple leaves is covered with numerous fine hairs which serve as a protection in keeping the spray solution away from the stomata. While no experimental evidence is offered at this time in support of the view that an increase in spreading power may induce more injury, the fact that spreaders are attracting considerable attention among horticulturists makes the factor of increased injury because of the lower surface tension worthy of consideration. This factor is merely mentioned for what it is worth as the spraying

tests in the orchard do not show any difference in the amount of injury from the solutions with and without spreaders.

In the tests for sulphur dioxide and hydrogen sulphide the moistened filter indicator papers and the test tubes containing the potassium iodate-starch, and lead acetate solutions the change from a colorless to a blue color is secured indicating the presence of the gases.

The apple leaves placed over the beakers of liquid lime sulphur show brown spotting similar to the usual lime sulphur injury under orchard conditions. Pleurococcus under the experimental conditions is not visibly affected as tests under the microscope with salt solution and distilled water show no appreciable difference.

It is found that liquid lime sulphur, boiled and at room temperatures, liberates a certain amount of minutely divided sulphur. In the experiments in which sediment is found in the distillate of the liquid lime sulphur, and in the test tube containing distilled water and connected by a delivery tube to unboiled liquid lime sulphur tests under the microscope with salt solution have no effect on single celled plants. Similar tests of thecheck plants in distilled water give a shrinking of thecontents of the cells. This goes to show that from liquid lime sulphur some

substance is given off in such a finely divided form as to be capable of killing the lower plants used. Dry flowers of sulphur alone seemingly do not possess this property. Indications are that lime when boiled with sulphur for the length of time followed in making lime sulphur breaks up some of the sulphur to very minute particles.

The microscopical examinations reveal a difference in size but not in form of the crystals of this finely divided precipitate given off from liquid lime sulphur and from flowers of sulphur. But since in the experimental work outlined the flowers of sulphur do not cause injury or bring about death of single celled plants the evidence is that the size of particle is of importance in this connection; the minute crystals are correlated with injury and killing, and the larger ones having no direct effect. For the flowers of sulphur to cause injury directly some change is necessary.

The acidity tests made by passing the sulphur dioxide and hydrogen sulphide gases into distilled water show but slight acid reactions. In the test with blue litmus water solution a duration of time of at least ten hours, keeping the liquid lime sulphur at a temperature just below the boiling point, is necessary for a distinct acid reaction.

The microchemical tests with barium chloride, of the apple leaves found to be injured when held over the liquid lime sulphur, and of the spray injured leaves taken from the orchard, do not indicate the presence of sulphates.

The experimental studies seem to indicate that lime sulphur injury may be caused in some undetermined manner by the action of sulphur dioxide, hydrogen sulphide, and very minute particles of sulphur.

Sulphuric Acid

The determinations made with litmus paper, barium chloride, sulphur-photometer, and the electro-metric hydrogenion apparatus show no indications of the presence of sulphuric acid.

When the aqueous solution of flowers of sulphur is tested with red litmus paper the change to a blue color is obtained. The test with Congo Red solution also shows a blue coloration.

It seems then that an aqueous solution of flowers of sulphur gives a decided acid reaction. This acid is shown by previously mentioned investigators to be sulphuric. Sulphuric acid is mentioned as being of some value as a fungicide. Observations of the sprayed plot in the orchard show that a 1-1000 dilution is injurious; the extent and

severity of the injury depending on weather conditions. The first application of the spray indicates but slight affectation but the injury increases with each successive spraying. The injury shows as a brownish coloration on the foliage; in the earlier applications the damage occurs about the margins of the leaves where the solution has collected before falling, the later sprays in addition to the above type cause a brown colored spotting and puckering wherever the solution has remained in contact with the leaf. Scab and insect injury are very prevalent showing that the value of sulphuric acid, 1-1000, as a fungicidal spray for apples is nil.

SUMMARY

1. The historical, laboratory, and orchard studies show that in attempting to explain lime sulphur injury the following theories should be borne in mind:

(a) The soluble polysulphides as the active agents.

(b) Absorption of the lime sulphur by the chlorophyll.

(c) Sunlight

(d) Heat

(e) Gas

(f) Acid

(g) Oxidation

(h) Minuteness of sulphur particles

2. Sunlight, heat, and oxidation may independently cause discoloration in leaves similar to lime sulphur injury. When exerting a detrimental effect at the same time as lime sulphur the injurious action is accelerated.

3. Experiments in the laboratory and observations in the orchard indicate that the factors conducive to, and correlated with the lime sulphur spray solution destruction of chlorophyll are high pressure, forcibly driven and coarse sprays, conditions leading to a thin epidermis, reduction

of pubescence, loose internal structure, presence of nascent oxygen, strong sunlight liberating actinic rays and heat, and subsequent final killing and oxidation of the tissues.

4. A microscopical examination of leaves damaged by lime sulphur indicates that the injury first appears as a slight russetting on the under surface. The injurious substance enters through the stomata and within 24 hours causes a brown coloration extending to the upper surface.

5. Very minute particles of sulphur are given off from liquid lime sulphur. Leaves and algae subjected to this form of sulphur are killed, while the comparatively large particles of finely divided flowers of sulphur exert no injurious effects under the experimental conditions. Apparently direct injury from sulphur is correlated largely with the minuteness of the size of particle.

6. Sulphur dioxide and hydrogen sulphide gases are liberated from liquid lime sulphur. These gases on combination with water give an acid reaction. The formation of acid from liquid lime sulphur from the union of these substances at room temperatures is very gradual.

7. Sulphuric acid could not be detected in appreciable quantities in, or as being liberated from lime sulphur. Apple fruits and leaves, however, when sprayed with sulphuric acid, 1-1000, show effects similar to lime sulphur injury.

8. Orchard trials show the fungicidal value of sulphuric acid, 1-1000, to be nil as fungus diseases and insect pests are not controlled. Extensive injury also occurs.

PART III

THE EFFECTS OF SPRAY FILMS OF LIME SULPHUR, ARSENATE OF LEAD, AND THE MIXTURE OF THE TWO, ON THE RATE OF GROWTH OF PLANTS.

The common knowledge that certain spray materials, i. e., Bordeaux mixture, cause an acceleration of growth, and others i. e., lime sulphur bring about a decrease or dwarfing in structure furnishes the working basis for this phase of the investigation. The modification in structure is totally distinct from the usual injurious effects, fungicidal values, and insecticidal properties of the compounds applied. The effects of transpiration and photosynthesis in this connection are studies and found to exert a considerable influence following the use of lime sulphur, arsenate of lead, and the mixture of the two.

It is well known that lime sulphur when sprayed on plants dwarfs the foliage. This belief is recognized to the extent that horticulturists have discontinued the use of this spray mixture on plants such as potatoes, tomatoes, and grapes. It must be understood that dwarfing is distinct in its meaning and differs from the term injury. In this paper injury is regarded as being correlated with insect pests, fungus diseases, and burning; and dwarfing as the restriction of normal growth.

While no attempt is made to present a complete resume of the literature on thesubject of dwarfing by lime sulphur, it is hoped that the few citations given below will illustrate that a decrease in growth of plants following the use of certain spray materials is a recognized fact.

On the dwarfing of plants by lime sulphur Clinton and French (15) may be cited as follows:

> "In the spring of 1910 Mr. Parrott, Station Entomologist, called attention to a pronounced dwarfing of early formed apple leaves due to the use of lime sulphur (1-40) in the Geneva Station orchard. The dwarfed leaves showed no lesions of any kind. They had not been burned by the spray."

Reed (55) writes in this manner: "In the spring when the leaves of certain varieties (of apple) are tender they may be dwarfed by the spray. This is usually done by applications before the trees bloom. Lime sulphur is especially likely to cause this dwarfing of the leaves."

Stewart and French (71) state that "Potato plants sprayed with lime sulphur were smaller than the check."

Hall (30) says: "In 1911-12 in tests at Geneva plants (potato) sprayed with lime sulphur were dwarfed by the fungicide, died early and yielded about 40 bushels less to the acre than plants in check rows."

Munn (51) related that "Rows of potatoes receiving six applications of lime sulphur died earlier than the check rows, while the same number of applications of bordeaux prolonged the life of the plants about two weeks and increased the yield of marketable tubers at the rate of 111.5 bu. per acre."

Sanders (62) Agr. Gazette, reports: "The season of 1915, on account of high winds and excessive moisture, gave rise throughout the Annapolis Valley to more

> scorching from lime sulphur than had previously occurred. Foliage sprayed with lime sulphur had a dwarfed and pale appearance even when not scorched."

Although the dwarfing of plants by lime sulphur solution is an acknowledged possibility, no explanation has been offered as yet that satisfactorily accounts for its occurrence.

Obviously, the dwarfing of a plant may be due either to an insufficient formation of substance necessary for growth and development, or loss of material already formed. The possibility also is presented of a detrimental process exerting a greater influence than a beneficial one and in this manner hindering growth.

THE EFFECT OF SPRAY FILMS ON THE FOLIAGE ON THE RATE OF TRANSPIRATION AND PERCENTAGE ORGANIC MATERIAL FORMED.

HISTORICAL

Transpiration

A survey of the literature shows that the work of the earlier investigators led them to the belief that decreased rates of transpiration followed spraying. Rumm (59) working with the grape saw that abscised sprayed leaves remained fresh longer than unsprayed, from which it is deduced that there was a falling off in transpiration as a result of spraying. Schander (66), using bordeaux mixture, the spray material employed by practically all the earlier researchers, suggests that lessened transpiration of sprayed leaves is due to the shading power of the spray. Müller-Thurgau and Bayer (7), also seem convinced that lessened transpiration followed spraying. Clinton (15) expresses the view that increased yield in potatoes is due to conservation of moisture by the clogging up of the stomata by the spray particles. Duggar (21) as the outcome of a visit to the Geneva Experiment Station, where Stewart in 1904 obtained an increase in yield of five times and a prolonging of life of twenty-five days in potato plants by the employment of Bordeaux, concurs with Clinton's view on the

clogging of the stomata.

On the other hand, Frank and Kruger (24) pronounce the opinion that since sprayed leaves are in general more robust, thicker, and stiffer than unsprayed that transpiration is accelerated by spraying. Bain (3) comes to the same conclusion in his work with peach trees, and perceives that the sprayed trees require the addition of more water to the soil about the roots than the unsprayed. Duggar and Cooley (21) in potometer and ptted plant experiments determine that certain sprays increase transpiration. Martin (44), independently proves the same thing and also mentions that the color of the film is a factor to be considered. His experiments illustrate that in abstised sprayed leaves, the average rate of water loss by transpiration attains an increase of 99 percent over the average rate for the standardization period. His results with potted plants are in the same direction but less in amount. Butler (10) shows that transpiration is increased by spraying with a 1 percent Bordeaux mixture solution. Shive and Martin (69) using the hygrometric paper method obtain indices of transpiration ranging from 18-29 percent higher for plant foliage treated with Bordeaux mixture.

Iljin (32) finds that the greatest transpiration independent of spray materials takes place 2 to 3 hours after

exposure to sunlight. Livingston and Brown (37) show that the maximum in relative transpiration occurs between the hours of 10:00 A. M. and 1:00 P. M. Bakke (2) working with Xanthium and Helianthus finds that the maximum average of transpiration appears at the 11th hour of the day.

Moisture Content

The percentage of water on a dry basis in the leaves of Fouquieria splendens is mentioned by Lloyd (38) as varying from 225 to 300 as extreme limits between day and night and that the diminution of water in the leaves begins at daybreak and continues until some time between noon and 4:00 P. M. After that time the water in the leaves increases until approximately 4:00 A. M. In experiments with the cotton plant Lloyd (39) finds that the leaf water stated in percentage of dry weight varies under usual conditions between 518 and 220 percent and that the minimum leaf water content is reached at 2:00 P. M. or thereabouts. The amount of water when thus determined is about 7 - 15 percent of the initial amount at sunrise.

Photosynthesis

It is realized that photosynthesis will be an important factor affecting the rate of growth of plants, in correlation with the application of the various spray solutions. The sprayed leaves having a much healthier color, a

greater transpiration, and hence a greater amount of manufactured material should be produced in accordance with the present theories in vogue.

Iljin (32) gives some interesting work closely related to this topic. He shows, although he does not use spray materials, that increased growth in plants may be due to a combination of transpiration and photosynthesis factors. He detects that the opening of the stomata is accompanied by the disappearance of starch from, as well as the development of high osmotic pressure in the guard cells, their closing by the appearance of starch being a fall in pressure. Conditions such as darkness which bring about closure of the stomata cause the conversion of the sugar in the guard cells into starch and the accompanying great fall in osmotic pressure; while the reverse processes occur on exposure to light and to conditions leading to moderate transpiration; in each case the time required for the processes in question is found to be about two hours. The rate of transpiration and the osmotic pressure in the guard cells correspond so closely that the curves expressing the two are shown by the author as being parallel.

In his studies with corn and sorghums Miller (47) finds that the maximum amount of dry matter in the leaves of the plants occurs in the most cases between 2:00 and 5:00 P. M.

METHODS OF EXPERIMENTATION

Transpiration

The plants used in the transpiration series are greenhouse tomatoes, Bonny Best variety, selected as uniform as possible from the number available. They range from 1½ to 2 feet in height, and possess the usual number of fruits characteristic of healthy plants at this stage of growth. They are grown in five inch pots placed inside galvanized iron containers, the top of which is covered with rubber cloth and fastened about the sides by means of wire. A glass tube is inserted through the covering for watering purposes and any openings remaining by which water may evaporate are blocked with paraffin. The plants are sprayed with a DeVilbiss No. 18 atomizer and weighings made on the Torsion balance every hour. The specimens are arranged in a row on a side bench and additional plants placed at each end for protection from surrounding external factors. Temperature, evaporation, humidity, and other such influences likely to affect the readings are not taken into direct account but an attempt is made to have the plants subjected to conditions uniform to all.

Readings, to ascertain the daily effect of the spray materials on transpiration in a test begun November

16, are made at 8:00 A. M. and again at 6:00 P. M. daily; giving values for sunshine and darkness periods. Lime sulphur when sprayed on tomato plants usually injures and dwarfs the foliage, therefore the trial is confined to a nine day comparison period for fear of influencing the results due to the harm caused the plant by this solution. The plants remain perfectly healthy throughout the experimentation period but show indications of damage one week after the completion of the test. Only four plants are used; one for each of the spray mixtures, and the fourth being sprayed with water and serving as the check.

In a method devised for calculating the transpiration values of table (13) eight classes are made based on surface area readings of tomato leaves obtained by means of the planimeter, converted to square centimetres, and multiplied by 0.0365 grams - the weight of one square centimetre of paper. Traced drawings of these classes of leaves are shown inpages following. Each leaf of the plant is compared in situ by being placed over the paper with the known areas drawn on. The estimate for each plant, serving as a base for the transpiration value is calculated by adding together the quantities obtained for each of the eight classes. The determinations as shown in Chart 5 should make the procedure clear.

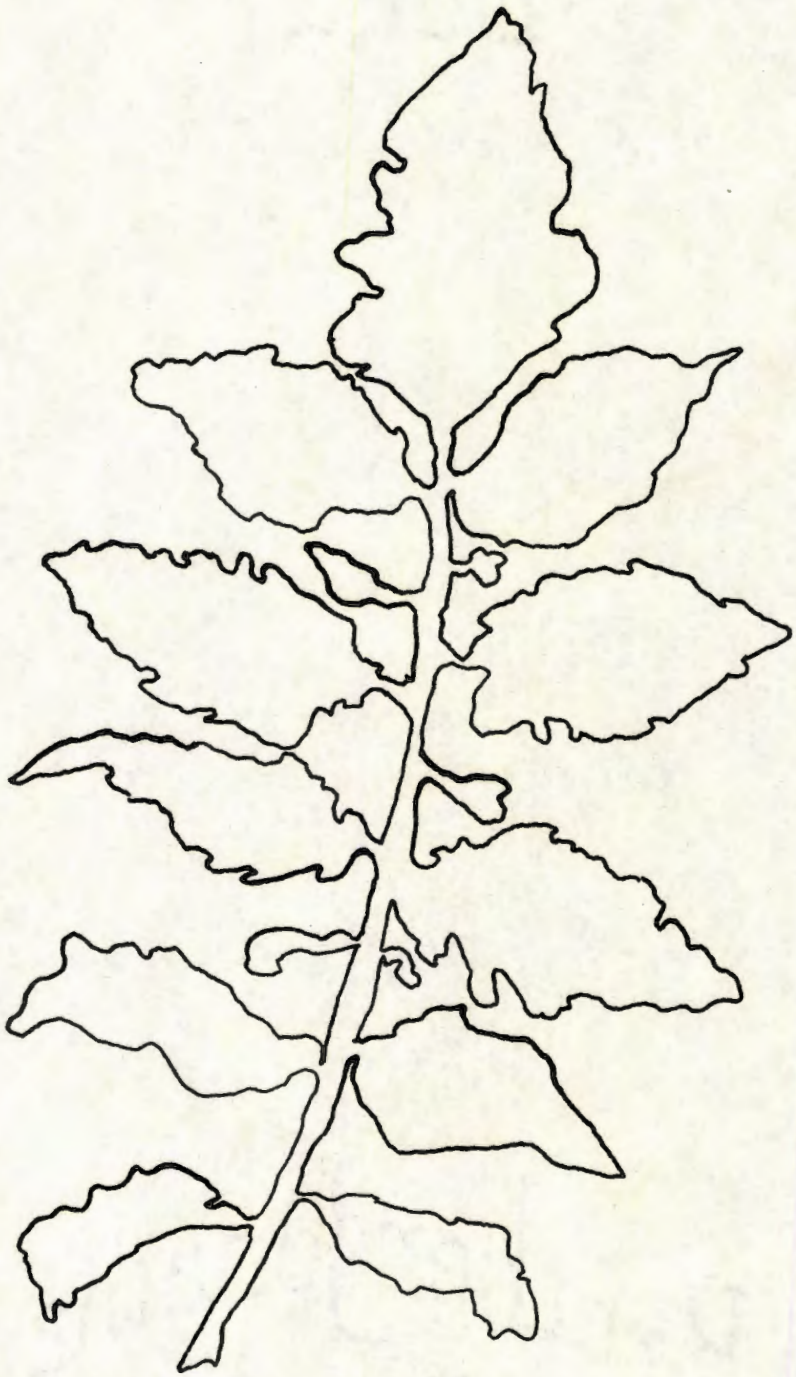
Class 1

Class 3

Class 2

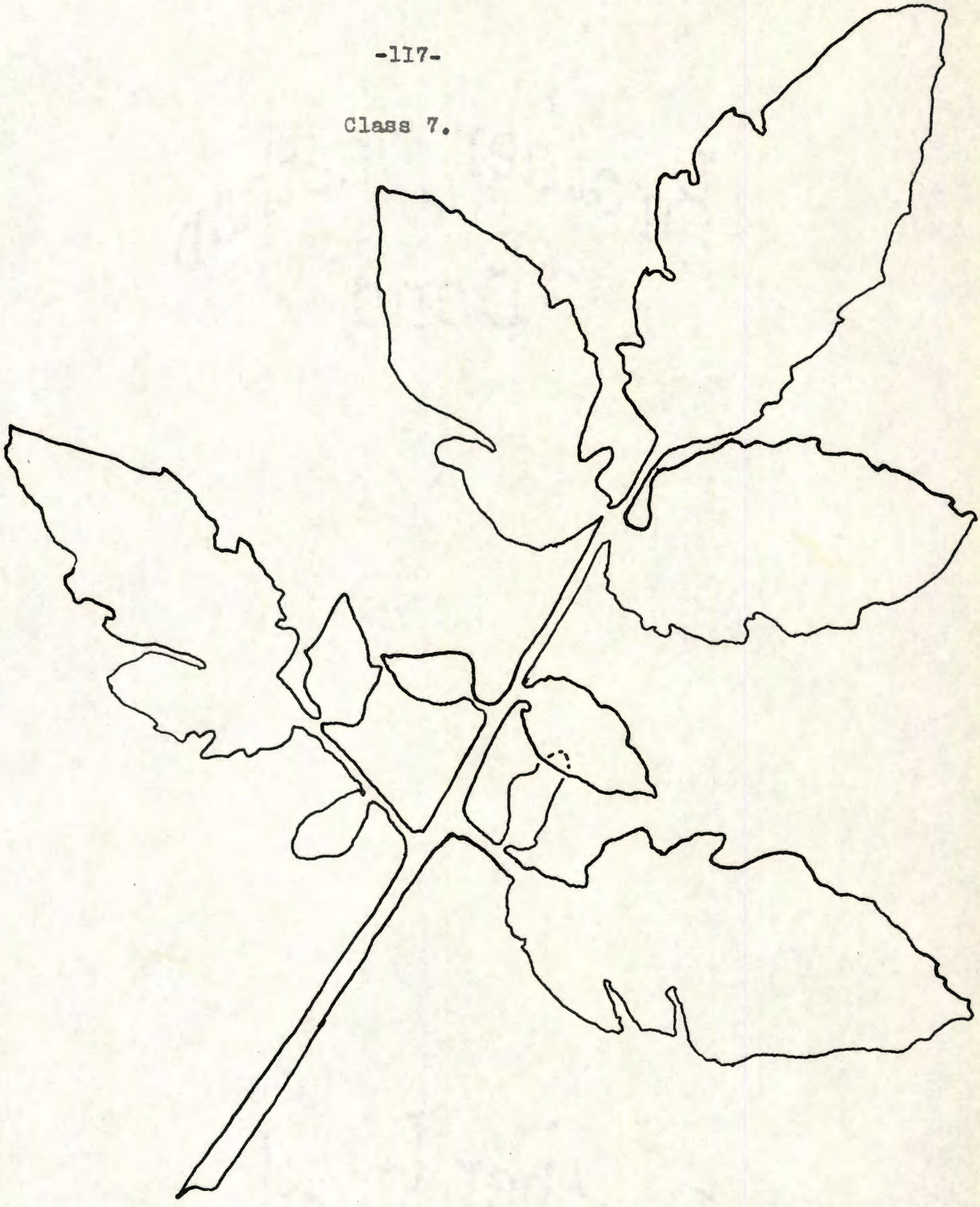
Class 4.

Class 5.



Class 6.

Class 7.



Class 8.

CHART 6 - ESTIMATION OF BASE FOR CALCULATION OF TRANSPIRATION VALUES.

Class	1	2	3	4	5	6	7	8
Average in sq. in.	5.0	9.4	13.2	17.8	23.6	30.0	37.4	45.0
	Number of Leaves							
Lime-Sulphur	16	5	5	3	1	5	4	2
Lead Arsenate	9	2	2	1	3	6	2	2
Lime Sulphur plus Lead Arsenate	4	0	0	5	1	0	4	2
Check	13	4	2	3	1	3	3	0

Total Grams per Plant

Lime sulphur	147.85
Lead arsenate	127.41
Lime sulphur plus lead arsenate	82.64
Check	99.13

N. B. - 100 sq. cm. = 15 sq. in.

1 " " = .0365 grams.

Moisture Content and Percentage Organic Material

To ascertain whether or not the conjecture as to the influence of the films on transpiration is correct a determination is made of the moisture content of the sprayed and unsprayed leaves at intervals of one hour throughout an eleven hour period.

Tomato plants growing in a permanent ground bed in the greenhouse are selected and sprayed with lime sulphur, arsenate of lead, and lime sulphur and arsenate of lead mixed. The sprayings are applied at 8:00 A. M. with an atomizer. Ten punchings are taken from each set of leaves every hour with a Bausch & Lomb one square centimetre leaf punch, care being taken to avoid the midribs. The punchings are collected in weighed test tubes which are immediately corked. The tubes containing sections of leaves are weighed on a balance sensitive to 0.0001 grams and steamed for ten minutes over a water bath. The series of material are dried in an oven at 100° C. until all the moisture is driven off. The samples are then cooled in a drying dessicator and re-weighed.

Four plants, as previously described, are used in the trial; one for each of the sprays, and the fourth as the check. Punchings are taken at hourly intervals on December 28. Data showing the result of the work are

shown in the table following, allowance being made for the weights of the various spray materials.

It is necessary in the transpiration tests, and moisture determinations, to have data at hand on the weight of the various spray mixtures. Hence a study of the three sprays used is made with this purpose in mind. Ordinary frosted glass as utilized in greenhouses is cut into squares 7 cm. on the sides, and thus giving a surface area of 49 sq. cm. The squares of glass are thoroughly dried in the electric oven and weighed. The material is sprayed on the rough surface by means of the atomizer. Soon after the film have dried the squares are again dried and the addition in weight recorded. The solutions are applied from the atomizer to four different angles by fifteen compressions of the bulb.

TABLE 12 - WEIGHT OF FILMS OF SPRAY MIXTURES IN GRAMS PER SQUARE CM.

Spray	90°	120°	155°	180°
Lime sulphur	.0001	.0001	.0002	.0002
Lead Arsenate	.0001	.0001	.0002	.0003
Lime sulphur plus Lead Arsenate	.0001	.0001	.0002	.0002
Check	.0000	.0000	.0000	.0000

TRANSPIRATION SERIES

TABLE 18 - SHOWING TRANSPIRATION IN GRAMS OF SPRAYED TOMATO PLANTS

Spray	Nov. 16 A. M. 8:00	Nov. 16 P. M. 6:00	Nov. 17 A. M. 7:30	Nov. 17 P. M. 7:00	Nov. 18 A. M. 8:00	Nov. 18 P. M. 6:30	Nov. 19 A. M. 9:00	Nov. 19 P. M. 6:00
Lime Sulphur	18.5	106.2	38.6	86.5	60.2	99.5	43.5	125.4
Lead Arsenate	18.2	100.5	35.5	83.5	58.1	86.5	44.7	148.2
Lime-Sulphur plus Lead Arsenate	17.1	97.5	40.5	76.2	64.5	113.8	46.2	150.5
Check	19.5	94.5	35.5	81.5	54.5	96.7	40.4	119.5

Spray	Nov. 20 A. M. 9:00	Nov. 20 P. M. 6:00	Nov. 21 A. M. 8:30	Nov. 21 P. M. 6:30	Nov. 22 A. M. 8:00	Nov. 22 P. M. 6:30	Nov. 23 A. M. 8:00	Nov. 23 P. M. 6:00	Nov. 24 A. M. 8:00	Nov. 24 P. M. 6:00
Lime Sulphur	50.5	104.4	49.5	116.2	45.6	119.8	45.3	119.8	52.3	117.6
Lead Arsenate	54.2	111.9	51.5	117.8	47.2	126.8	43.5	132.5	46.5	129.3
Lime-Sulphur plus Lead Arsenate	56.4	109.5	54.4	124.3	48.2	130.5	43.1	133.2	51.6	126.5
Check	52.3	92.6	42.5	103.6	46.6	96.7	41.5	101.2	48.6	96.7

TABLE 14 - PERCENTAGE INCREASE IN DAILY TRANSPIRATION CALCULATED ON RATE.

	Date	Lime Sulphur	Lead Arsenate	Lime Sulphur plus Lead Arsenate	Check
*	Nov. 16	0.00	0.00	0.00	0.00
*	Nov. 17	0.00	0.00	0.00	0.00
	Nov. 18	27.21	21.55	54.19	32.05
	Nov. 19	35.34	63.21	70.13	39.48
	Nov. 20	23.16	39.65	43.64	35.28
	Nov. 21	32.77	42.42	56.45	27.59
	Nov. 22	31.73	46.38	56.44	25.07
	Nov. 23	30.69	47.89	52.64	24.43
	Nov. 24	36.14	47.89	54.19	26.89

* Standardization values.

Form E-4

GRAPH 111.

From a perusal of tables (13 and 14), and from Graph (111), it is evident that the application of solutions of arsenate of lead, and a mixture of lime sulphur and arsenate of lead has caused an increase in transpiration. The lime sulphur alone has had little or no effect on the rate of water loss.

Transpiration values considered according to the method outlined previously are computed at different times of the day; readings being taken at periodic intervals of one hour.

A - actual transpiration in grams.

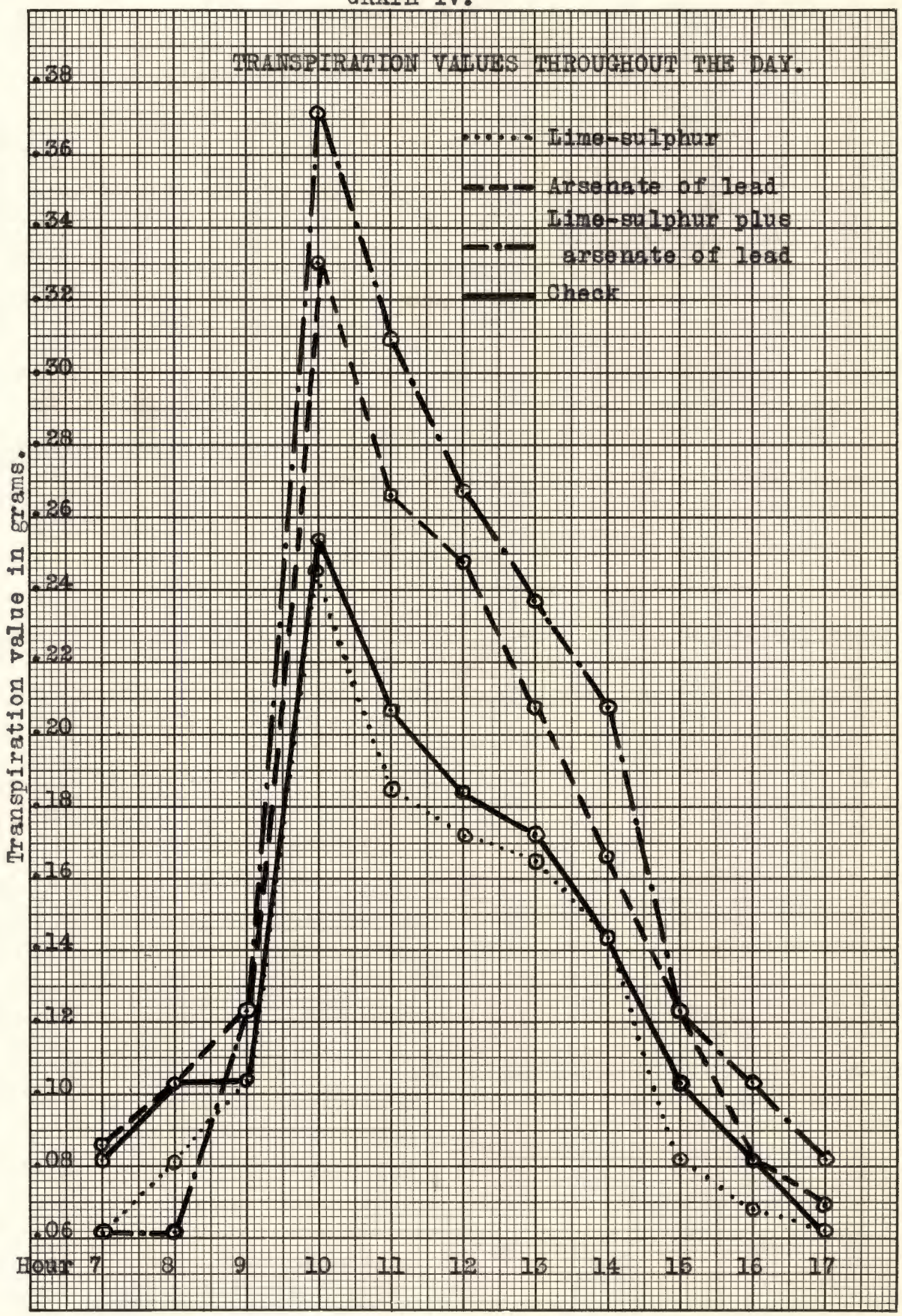
B - transpiration value in grams.

TABLE 16 - TRANSPIRATION VALUES THROUGHOUT THE DAY.

Hour	Lime Sulphur		Lead Arsenate		Lime Sulphur plus Lead Arsenate		Check	
	A	B	A	B	A	B	A	B
7	9.1	.062	10.9	.086	7.6	.062	6.1	.092
8	12.2	.082	13.1	.103	8.4	.062	6.2	.101
9	15.2	.103	18.7	.123	9.5	.122	12.3	.103
10	36.5	.247	41.9	.329	20.9	.371	36.7	.253
11	27.4	.185	34.1	.267	16.1	.309	30.6	.206
12	25.5	.172	31.4	.247	15.2	.267	26.5	.184
13	24.3	.164	26.2	.206	14.1	.247	24.5	.171
14	21.3	.144	23.6	.165	13.3	.206	20.4	.144
15	12.2	.082	15.7	.122	8.5	.122	12.2	.103
16	10.3	.069	13.1	.103	7.6	.082	8.2	.082
17	9.1	.062	10.5	.082	5.7	.069	6.9	.062

Form E-4

GRAPH IV.



From a study of table (15), and graph (IV) it is seen that the greatest water loss occurs at the end of the10th hour, 11 o'clock. That some acceleration is given from the use of lime sulphur and arsenate of lead mixed, and from the arsenate of lead alone is evident. The lime sulphur alone has little or no effect in this respect.

TABLE 16 - MOISTURE CONTENT OF SPRAYED TOMATO LEAVES.

LIME SULPHUR

Hour	Green Wt.	Dry Wt.	Wt. Water (calc.)	% Water on Dry Wt.	% Water on Green Wt.
7	.1632	.0311	.1321	425	80.95
8	.1614	.0308	.1306	424	80.91
9	.1600	.0307	.1292	421	80.75
10	.1384	.0282	.1102	391	79.77
11	.1364	.0298	.1075	372	78.85
12	.1286	.0278	.1008	359	78.30
13	.1249	.0275	.0974	354	77.98
14	.1209	.0268	.0940	351	71.81
15	.1438	.0290	.1148	396	79.85
16	.1457	.0288	.1149	399	79.96
17	.1466	.0291	.1155	397	79.79

ARSENATE OF LEAD

Hour	Green Wt.	Dry Wt.	Wt. Water (calc.)	% Water on Dry Wt.	% Water on Green Wt.
7	.1617	.0308	.1309	425	80.95
8	.1598	.0305	.1295	424	80.91
9	.1608	.0309	.1299	420	80.72
10	.1386	.0284	.1102	388	79.51
11	.1305	.0282	.1023	363	78.54
12	.1256	.0276	.0980	355	78.03
13	.1200	.0265	.0935	353	77.92
14	.1399	.0297	.1102	376	78.77
15	.1459	.0297	.1162	398	79.95
16	.1401	.0285	.1116	395	79.96
17	.1471	.0296	.1175	397	79.88

LIME SULPHUR PLUS ARSENATE OF LEAD

Hour	Green Wt.	Dry Wt.	Wt. Water (calc.)	% Water on Dry Wt.	% Water on Green Wt.
7	.1612	.0307	.1305	425	80.96
8	.1621	.0310	.1311	423	80.88
9	.1549	.0296	.1245	420	80.25
10	.1414	.0291	.1123	386	79.42
11	.1304	.0286	.1018	356	78.07
12	.1199	.0269	.0930	346	77.57
13	.1195	.0268	.0927	346	77.57
14	.1359	.0295	.1064	361	78.50
15	.1497	.0302	.1177	394	79.29
16	.1471	.0299	.1172	392	79.68
17	.1462	.0294	.1168	394	79.89

CHECK

Hour	Green Wt.	Dry Wt.	Wt. Water (calc.)	% Water on Dry Wt.	%Water on Green Wt.
7	.1629	.0310	.1319	425	80.97
8	.1609	.0307	.1302	424	80.92
9	.1599	.0305	.1294	421	80.91
10	.1383	.0281	.1102	392	79.61
11	.1305	.0280	.1025	366	78.54
12	.1256	.0275	.0981	357	77.99
13	.1233	.0271	.0962	355	77.94
14	.1388	.0294	.1094	372	78.82
15	.1477	.0296	.1181	399	79.95
16	.1464	.0294	.1170	398	79.92
17	.1451	.0292	.1159	397	79.87

From the figures as given it appears that the minimum moisture content of the leaves occurs at the 13th hour. It seems also that the moisture content decreases from daybreak until the 13th hour, and then tends to increase again.

The data obtained affords a means of comparison with the work of previous workers, with and without the application of films of spray materials, and as a source of information for revealing the effect of the dispersion of the liquid on the foliage.

Some idea of the amount and rate of transpiration due directly to the consequence of the applications of the spray materials, and the moisture content of the leaves at hour intervals of the day having been secured, it is believed that there is sufficient reason to presume that such conditions as dwarfing may be partly explained by extending the investigation to a determination of the amount of organic material formed in the leaves.

Table (17) is applied to show the amount of organic material in the leaf formed during the day.

TABLE 17 - PERCENTAGE ORGANIC MATERIAL FOUND IN LEAVES DURING THE DAY.

Hour	Lime Sulphur	Lead Arsenate	Lime Sulphur plus Lead Arsenate	Check
7	19.06	19.06	19.04	19.05
8	19.08	19.08	19.12	19.08
9	19.19	19.22	19.12	19.08
10	20.38	20.49	20.58	20.32
11	21.18	21.68	21.93	21.46
12	21.62	21.97	22.44	21.88
13	22.02	22.09	22.45	21.98
14	20.47	21.23	21.70	21.18
15	20.16	20.36	20.42	20.12
16	20.04	20.34	20.34	20.08
17	19.85	20.12	20.34	20.04

GRAPH V - PERCENTAGE ORGANIC MATERIAL AT HOUR INTERVALS DURING THE DAY.

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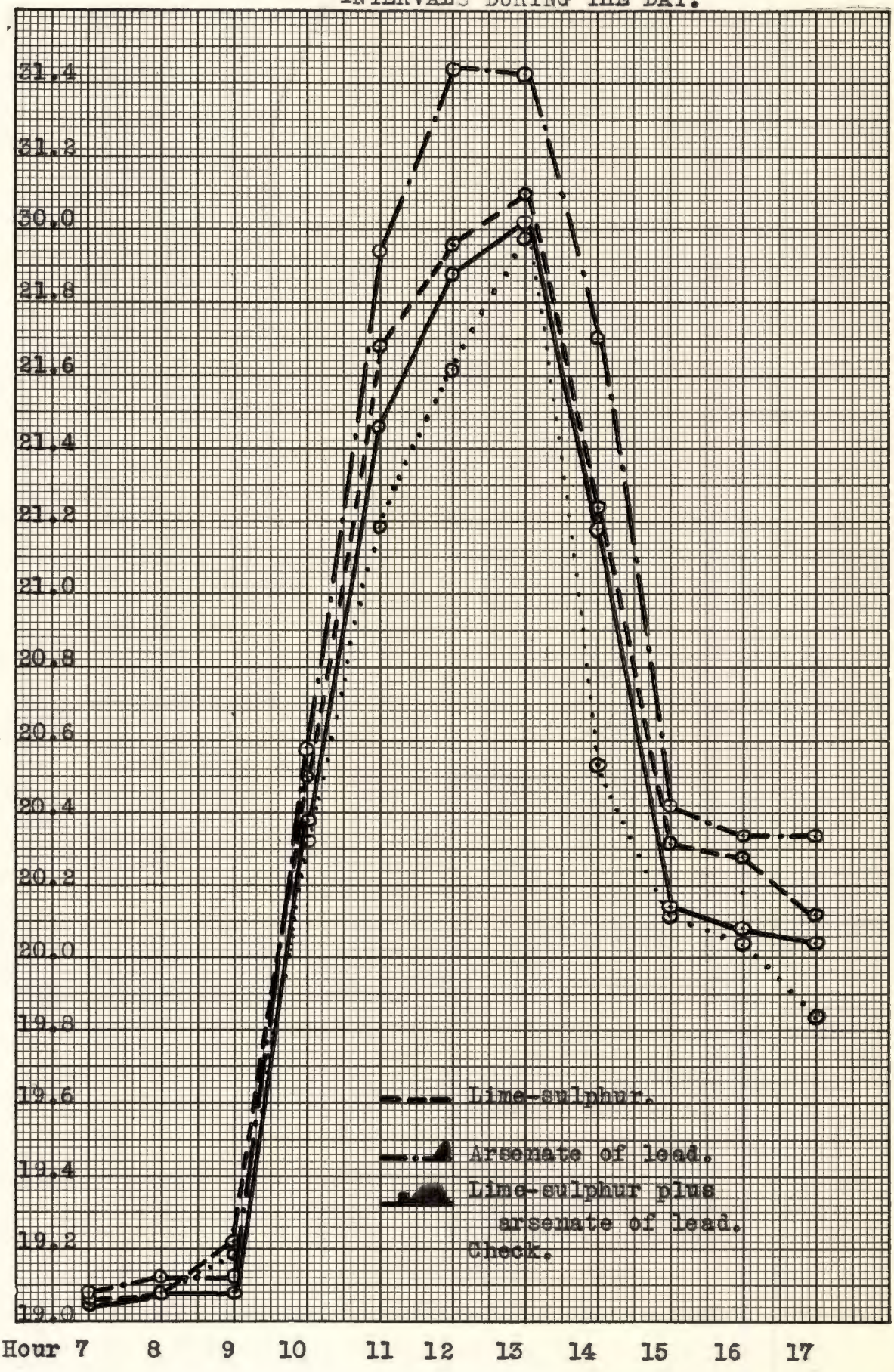
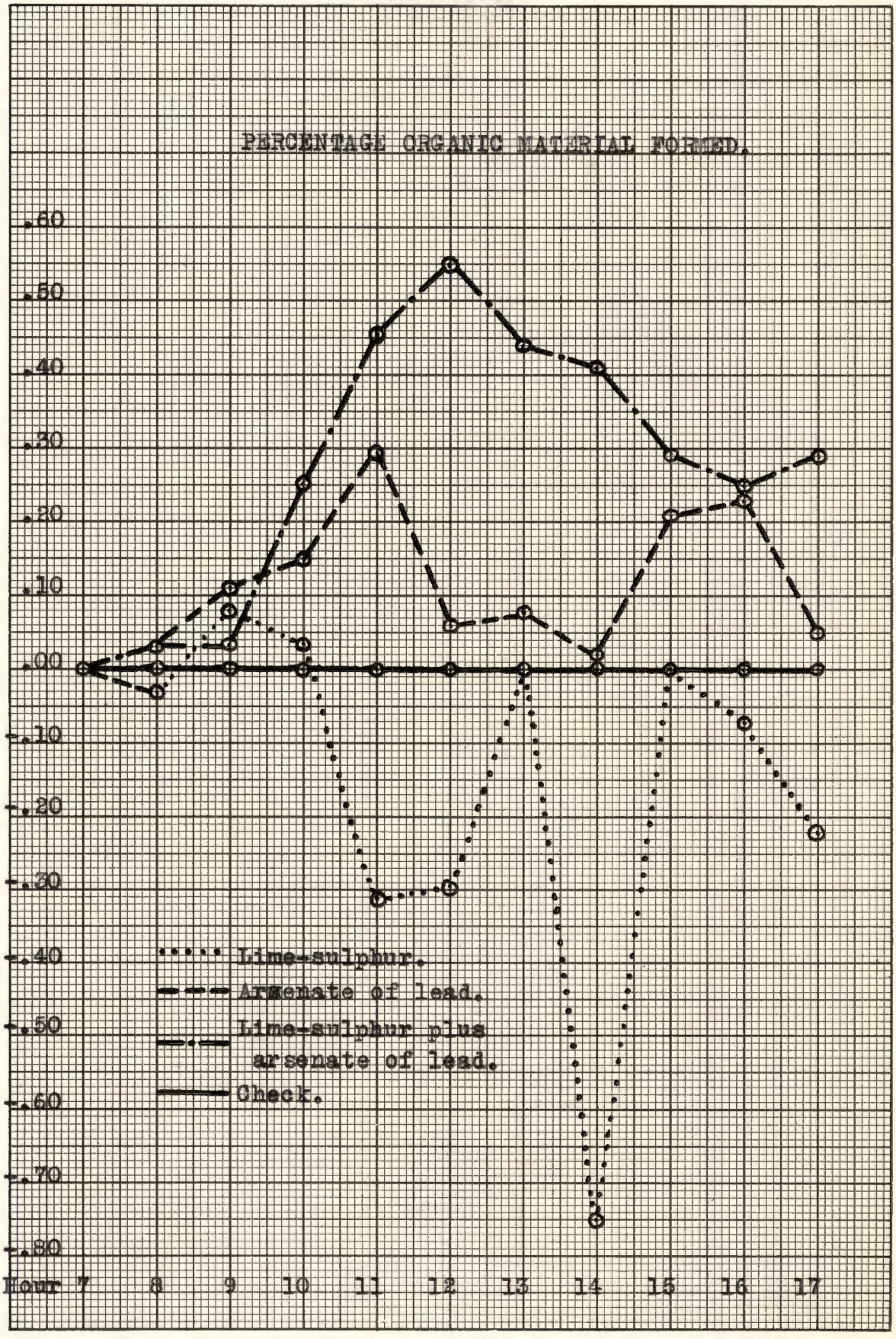


TABLE 18 - INFLUENCE OF SPRAY MATERIALS UPON FORMATION OF ORGANIC MATERIAL IN THE LEAVES - PERCENTAGE RATE AT CORRESPONDING HOUR

Hour	Lime Sulphur	Lead Arsenate	Lime Sulphur plus Lead Arsenate
7	.00	.00	.00
8	.03	.03	.03
9	.08	.11	.05
10	.03	.14	.25
11	- .31	.29	.46
12	- .29	.06	.55
13	.01	.08	.44
14	- .74	.02	.41
15	.01	.21	.29
16	- .07	.25	.25
17	- .22	.05	.29

Form E-4

GRAPH VI.



The data for table (17) are compiled under conditions when the plants are exposed to bright sunshine. Under such influences in the greenhouse it is apparent that the percentage of organic material formed in the foliar parts of the plant is greatest at the 13th hour, or 1 o'clock. The series for each plant increases from daybreak until this time, and then decreases again. The decrease in the percentage of organic material formed seems to be a factor worthy of consideration in seeking for an explanation of the dwarfing effect of lime sulphur on plants.

The experimental data secured indicates that the lime sulphur solution alone has little influence on the rate of transpiration in tomato plants, but decreases the percentage of organic material formed in the leaves. On the other hand, arsenate of lead alone, and the combination spray of arsenate of lead and lime sulphur increase the rate and amount of transpiration and also the amount of organic material in the foliage.

It is pointed out by Crandall (17) that the molecular concentration of the fruit of fruit trees is generally less than that of the leaves. He believes that such a condition enables the leaves to remove water from the fruit.

Observation of green apples of one-half inch diameter after being sprayed with the usual orchard combination spray of lime sulphur and arsenate of lead show that when the fruit and attached twigs and leaves are cut from the tree a shrivelling and drying out of the apples quickly occurs. Since Jost (34) quotes Bouissingault as authority for the fact that apples provided with a normal cuticle lose but 0.005 grams of water per hour from a square centimeter of normal apple surface, it is possible that the shrinkage perceived in the case of the small green apples is due to water movement from the fruit to the leaves, and subsequent accelerated loss by transpiration through the numerous stomata on the underside of the leaf. The higher the percentage of organic material in the leaves the more rapidly would this loss of water from the fruit take place.

The results of the study indicate that transpiration and photosynthesis are factors influencing the rate of growth of plants. The limited data at hand does not warrant definite conclusions as to how the dwarfing or so-called stimulating effects are brought about. The data may be of some value should further work be done and

is presented for this reason, and because of the fact that the general influences perceived may be of some aid in the selection of the most favorable spray material for orchard use.

SUMMARY

1. Spray films of lime sulphur, arsenate of lead, and the combination of the two, exert an influence on the rate of growth of plants; being distinct in this respect from their fungicidal and insecticidal actions.

2. Transpiration and photosynthesis are two factors closely concerned with this modification in structure.

3. Aqueous solutions of arsenate of lead, and of arsenate of lead and lime sulphur mixed, when applied to the foliage of plants, cause an increase in transpiration. Lime sulphur solution alone has little effect.

4. The greatest transpiration in this investigation, takes place two to three hours after spraying, or at 11 o'clock independent of spraying.

5. The minimum water content of the leaves occurs at about 1 o'clock. The percentage moisture in the leaves decreases from daybreak until this time, and then increases again.

6. When a spray film of lime sulphur is applied to the foliage of tomato plants less organic material is formed, other factors being equal, than when

water is applied as the spray. Arsenate of lead, and the mixture of lime sulphur and arsenate of lead increase the amount of organic material formed, during the same length of time and under similar external conditions.

7. The rate of growth of plants following applications of the spray mixtures is influenced by the amount of water transpired, and the amount of materials formed by photosynthesis in the leaves.

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